

Express Mail Number: EL052827287US

Docket No. B-3643 617072-2

Date: April 26, 1999

Commissioner of Patents and Trademarks  
Box Patent Application  
Washington, D.C. 20231

Sir:

**NEW APPLICATION TRANSMITTAL**

Transmitted herewith for filing is the patent application of

Inventor(s): (1) **ANTONIO MUÑOZ-ESCALONA LAFUENTE**

(2) **PILAR LAFUENTE CAÑAS**

(3) **JOSE SANCHO ROYO**

(4) **BEGOÑA PEÑA GARCIA**

(5) **CARLOS MARTIN MARCOS**

NOTE: Patent must be applied for in the name of all  
of the actual inventor or inventors.

For: **CATALYTIC SYSTEMS FOR THE POLYMERIZATION AND  
COPOLYMERIZATION OF ALPHA-OLEFINS**

Enclosed are:

**The Papers Required For Filing Date Under 37 CFR 1.53(b):**

63 Pages of specification 2 Pages of abstract 4 Pages of claims

1 Sheet of drawings [X] formal [ ] informal

[X] In addition to the above papers there is also attached  
1 Page of an amendment dated April 26, 1999.

Check for filing fee in the amount of \$760.00

Declaration/Power of Attorney (4 Pages)

Assignment Cover Sheet, Assignment document, and Check for \$40.00  
Postcard

**CERTIFICATION UNDER 37 CFR 1.10**

I hereby certify that this paper and the documents referred to as enclosed  
therein are being deposited with the United States Postal Service in an Express  
Mail envelope with sufficient postage for Express Mailing on this date April 26,  
1999 in an envelope as "Express Mail Post Office to Addressee" Mailing Label  
Number EL052827287US addressed to the:

Commissioner of Patents and Trademarks  
Box Patent Application  
Washington, D.C. 20231

Alex Martinez

(Typed or printed name of person mailing paper)

(Signature of person mailing paper)

NOTE: Each paper or fee referred to as enclosed herein  
has the number of the "Express Mail" mailing label  
placed thereon prior to mailing. 37 CFR 1.10(b).

## 2. Declaration or oath

☒ Enclosed

☒ original ☐ facsimile

executed by:

☒ inventor(s)

☐ legal representative of inventor(s) 37 CFR 1.42 or 1.43

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached. 37 CFR 1.47.

☐ petition and statement required by 37 CFR 1.47 also attached. See item 7 below for fee.

☐ Not Enclosed

☐ Application is made by a person authorized under 37 CFR 1.41<sup>6</sup> on behalf of all of the above named inventor(s). The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently.

☐ Showing that the filing is authorized. (Not required unless called into question. 37 CFR 1.41(d)).

NOTE: Where the filing is a completion in the U.S. of an international application under 35 U.S.C. 371(c)(4) then the declaration must be filed.

## 3. Assignment

☒ An assignment of the invention to REPSOL QUIMICA S.A.  
(With separate cover sheet and check for \$40.00)

## 4. Certified Copy

☐ A certified copy of application(s) \_\_\_\_\_

from which priority is claimed.

NOTE: Must be referred to in oath or declaration. 37 CFR 1.55 and 163.

## 5. Fee Calculation

CLAIMS AS FILED			
Number Filed	Number Extra	Rate	Basic Fee \$ 760.00
Total Claims 9 -20=	x	\$ 18.00	
Independent Claims 2 -03=	x	\$ 78.00	
Multiple Dependent Claim(s), If Any	x	\$260.00	

☐ Amendment cancelling extra claims enclosed

☒ Amendment deleting multiple dependencies enclosed

☐ Fee for extra claims is not being paid at this time

NOTE: If the fee for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency, 37 CFR 1.16(d).

Filing Fee Calculation \$ 760.00

6. Small Entity Statement

☐ Verified statement that this is a filing by a small entity under 37 CFR 1.9 and 1.27.

Filing Fee Calculation (50% of above) \$ \_\_\_\_\_

NOTE: If a verified statement is filed within 2 months of the date of payment of first fee then the excess fee paid will be refunded on request. Notice of January 20, 1983. 1027 TMOG 114.

7. Fee Payment Being Made At This Time

☐ Not Enclosed

☐ No filing fee is submitted. This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.

NOTE: Where the filing is a completion in the U.S. of an international application the fee must be paid.

☒ Enclosed

☒ filing fee \$ 760.00

☐ recording assignment \$ \_\_\_\_\_  
(\$40.00; 37 CFR 1.21(h)(I))

☐ petition fee for filing by other than  
all the inventors or person on behalf  
of the inventor where inventor refused  
to sign or cannot be reached.  
37 CFR 1.47 and 1.17 (h) \$ \_\_\_\_\_

Total fees enclosed \$ 760.00

8. Method of Payment of Fees

☒ check in the amount of \$ 760.00

☐ charge account No. 12-0415 in the amount of \$ \_\_\_\_\_  
A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

9. Authorization to Charge Additional fees

☒ The Commissioner is hereby authorized to charge the following additional fees which may be required to Account No. 12-0415:

☒ 37 CFR 1.16 (filing fees and presentation of extra claims)

☒ 37 CFR 1.17 (application processing fees)

☐ 37 CFR 1.18 (issue fee at or before Mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))


NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application...prior to paying... issue fee".

10. Instructions As To Overpayment

☒ Credit Account No. 12-0415 ☐ refund

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Richard P. Berg  
Attorney for the Applicant  
Reg. No. 28,145

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Antonio Muñoz Escalona, et al.

Serial No.:	)	Re: Preliminary Amendment
	)	
Filed: Concurrently herewith	)	Our Ref: B-3643 617072-2
	)	
For: "CATALYTIC SYSTEMS FOR THE POLYMERIZATION AND COPOLY- MERIZATION OF ALPHA-OLEFINS"	)	Date: April 26, 1999

Hon. Commissioner of Patents and Trademarks  
Box Patent Application  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, it is respectfully requested that the following amendments be made to the claims:

IN THE CLAIMS

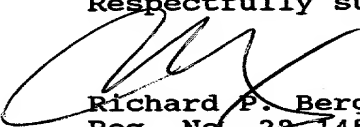
PLEASE RENUMBER CLAIMS 6-10 AS CLAIMS 5-9.

Claim 3, line 1	Please change "claims 1-3" to-- claim 1--.
Claim 4, line 1	Please change "claims 1-4" to-- claim 1--.
Newly renumbered Claim 5, line 1	Please change "claims 1-5" to--claim 1--.
Newly renumbered Claim 6, line 1	Please change "claims 1-6" to--claim 1--.
Newly renumbered Claim 7, line 1	Please change "7" to --6--.
Newly renumbered Claim 8, line 2	Please change "claims 1-8" to--claim 1--.

REMARKS

The amendments set forth above renumbers claims 6-10 as claims 5-9 and delete the multiple dependencies from Claims 3, 4, and newly renumbered Claims 5, 6, 7, and 8. The applicant may add additional claims or sub-claims to provide coverage similar to, broader than, or narrower than the present claims at any time during the pendency of the above-identified U.S. application.

Respectfully submitted,

  
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Attorney for Applicant

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## CATALYTIC SYSTEMS FOR THE POLYMERIZATION AND COPOLYMERIZATION OF ALPHA-OLEFINS

The present invention relates to a heterogeneous catalytic system and its use in olefin polymerization.

### 5      **STATE OF THE ART**

It is very well known that homogeneous catalytic systems present a disadvantage: when they are used in suspension polymerization processes, a part of the produced polymer adheres to the reactor walls; this effect is technically called "reactor fouling". Besides, in most cases, the particle size of the obtained polymer is very small and the bulk density is  
10      low, thus the industrial production is reduced. In order to prevent the reactor from fouling and to control the size and the morphology of the polymer particles which are formed, the homogeneous system can be supported on an inorganic oxide.

In the last years different preparatory strategies have been used in order to reach this aim. EPA-206794 (Exxon) discloses a catalyst which comprises a carrier, a metallocene, and  
15      an alumoxane. The carrier is first treated with alumoxane and then the metallocene is added. EP-A-295312 (Mitsui) discloses a catalyst consisting of a carrier wherein alumoxane is precipitated and then the resulting material is impregnated with a metallocene. No additional cocatalyst is used in the polymerization process.

The first application claiming a process wherein the metallocene is reacted with the  
20      support surface is EP 293815 (HOECHST). The metallocene contains a SiOR group that reacts with the OH groups on the surface of the support.

EP 757053 (HOECHST) supports the metallocene by reacting the hydroxy groups of the inorganic support with a metallocene which contains a M-R-Z-Cl group, wherein M is Si, Ge or Sn and Z is B, Si, Ge or Sn. EP 757992 (REPSOL) discloses a catalyst comprising a  
25      metallocene which contains a Si-Cl group to react with the hydroxyls of the inorganic support.

Object of the present invention is the preparation of a supported catalyst for (co)polymerization of ethylene, whose activity is not decreased by the heterogeneization process and which results in a polymer having a very good morphology.

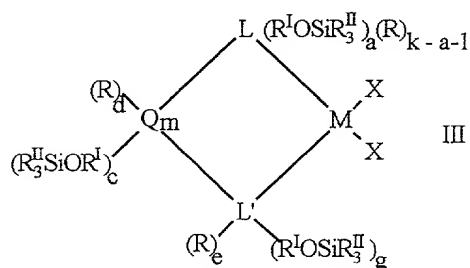
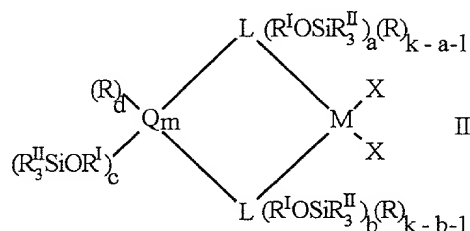
Thanks to the methods described in the present invention, heterogeneous catalysts can  
30      be obtained; they allow to effectively control the morphology and the distribution of particle sizes, with a regular growth of the polymer around the catalyst particles and without reactor fouling.

### **DETAILED DESCRIPTION OF THE INVENTION.**

35      The present invention relates to heterogeneous catalytic systems obtained by reacting a

specific class of metallocene compounds with a treated porous inorganic support, i.e. a support having on its surface an alumoxane.

According to the present invention the specific class of metallocene compounds is defined by general formulas I, II and III.



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl and benzoidenyl;

each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>;

each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>;

each R<sup>II</sup> is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably

R<sup>II</sup> is methyl, ethyl, isopropyl;

each **Q** is independently selected from B, C, Si, Ge, Sn; preferably it is C or Si;

**M** is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide; preferably it is titanium, zirconium or hafnium;

each **X** is independently selected from: hydrogen, chlorine, bromine,  $\text{OR}^{\text{II}}$ ,  $\text{NR}^{\text{II}}_2$ ,  $\text{C}_1\text{-C}_{20}$  alkyl or  $\text{C}_6\text{-C}_{20}$  aryl; preferably it is chlorine, bromine;

**L'** is N or O;

**k** depends of the type of **L**; more specifically when **L** is cyclopentadienyl **k** is equal to 5, when **L** is indenyl **k** is equal to 7, when **L** is fluorenyl or benzoindenyl **k** is equal to 9, when **L** is tetrahydroindenyl **k** is equal to 11 and when **L** is octahydrofluorenyl, **k** is equal to 17;

**z** is equal to 0, 1 or 2; preferably **z** is 1;

**x** is equal to 1, 2 or 3; preferably **x** is 1;

**y** is equal to 1, 2 or 3;

**x + y + z** is equal to the valence of **M**;

**m** is an integer which can assume the values 1, 2, 3 or 4;

**a** and **b** are integers whose value ranges from 0 to **k**-1;

**f** is an integer whose value ranges from 1 to **k**;

**g** is an integer whose value ranges from 0 to 1;

**c** and **e** are equal to 0 or 1;

**a + b + c** is at least 1;

**a + g + c** is at least 1;

**d** is equal to 0, 1 or 2;

when **Q** is B, then **c + d** = 1;

when **Q** is C, Si, Ge or Sn, then **c + d** = 2;

when **L'** is N, then **g + e** = 1;

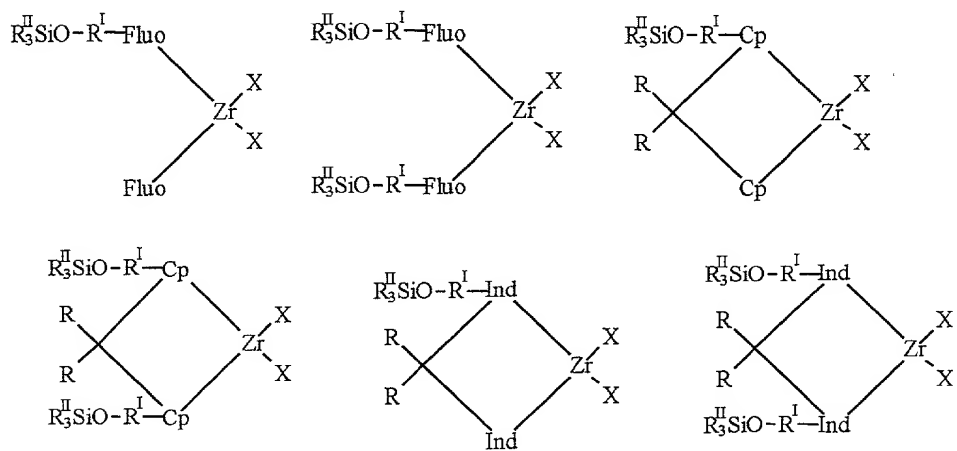
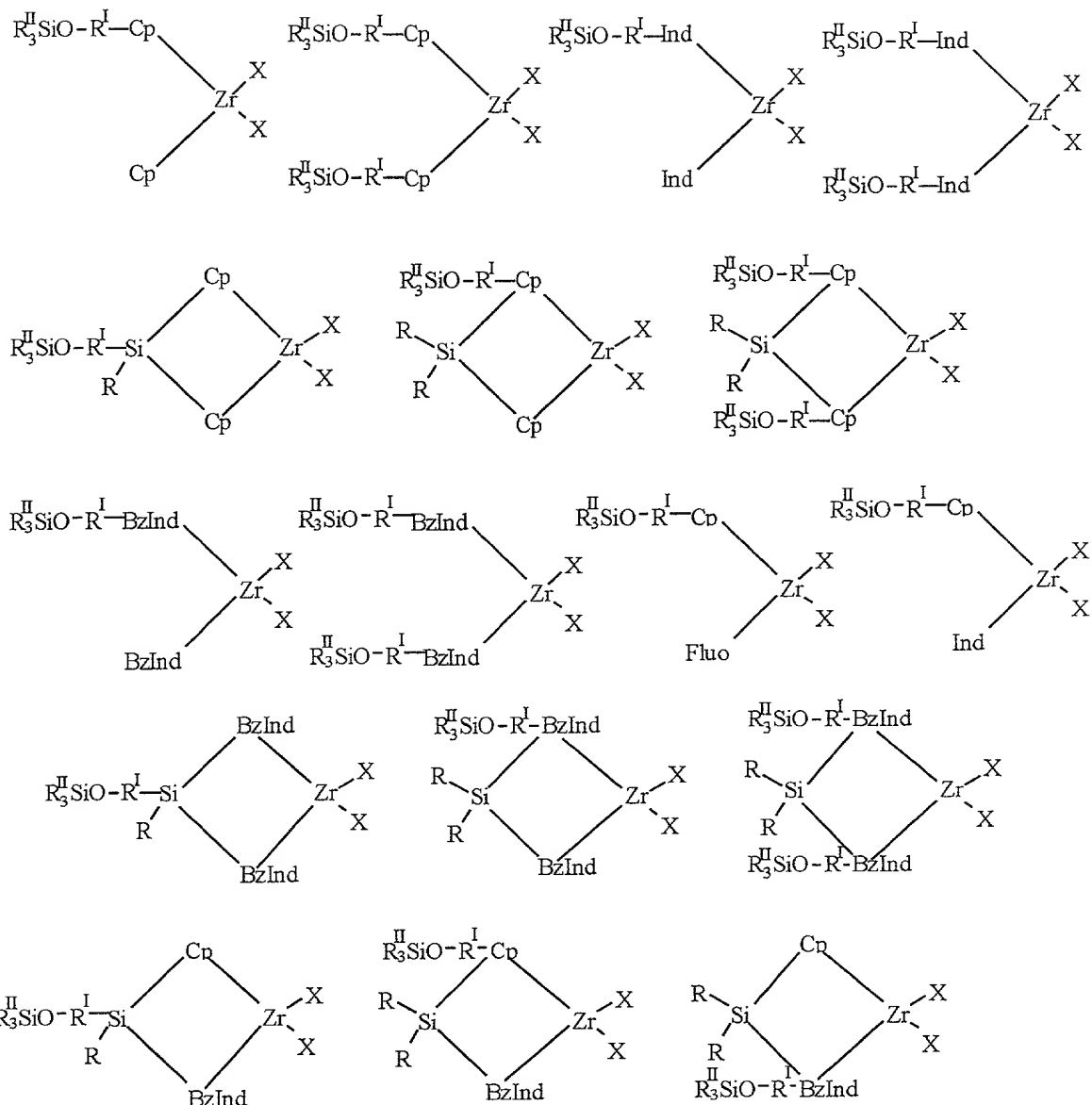
when **L'** is O, then **g** = 0 and **e** = 0.

Non limitative examples of  $\text{R}^{\text{I}}\text{OSiR}^{\text{II}}_3$  are:

$\text{CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH}_2\text{-O-CH}_2\text{-OSiMe}_3$ ;  $\text{O-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  
 $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  
 $\text{CH}_2\text{-C}_5\text{H}_5\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH(C}_2\text{H}_5\text{)-CH}_2\text{-OSi(C}_2\text{H}_5\text{)}_2\text{Me}$ ;  $\text{C(CH}_3\text{)}_2\text{-C(CH}_3\text{)}_2\text{-OSi(PhMe)}_3$  ;  
 $\text{CH(CH}_3\text{)-CH(CH}_3\text{)-O-SiEtMe}_2$ ;  $\text{SiMe}_2\text{-OSiMe}_3$ .

Preferably the group  $\text{R}^{\text{I}}\text{OSiR}^{\text{II}}_3$  is selected from  $\text{CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{CH}_2\text{-O-CH}_2\text{-OSiMe}_3$ ,  $\text{O-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{SiMe}_2\text{-OSiMe}_3$ ;  $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ .

Preferred structures of compounds of formula I, II and III are the following:





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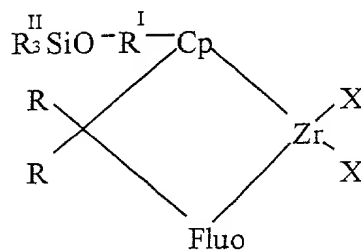
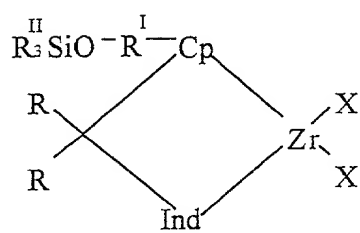
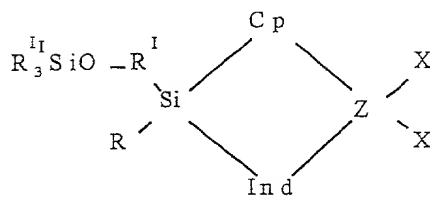
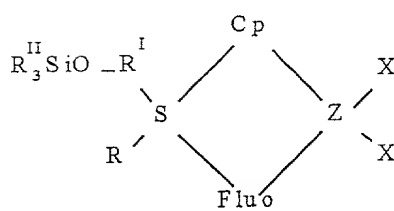
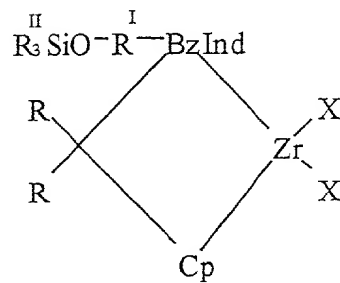
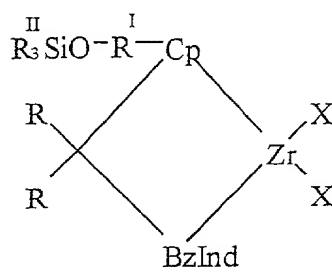
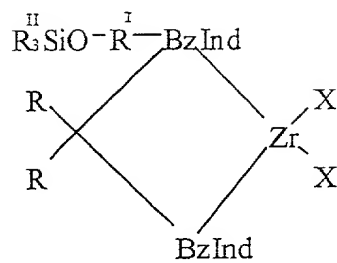
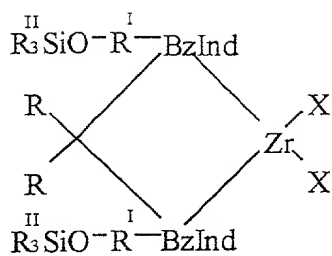
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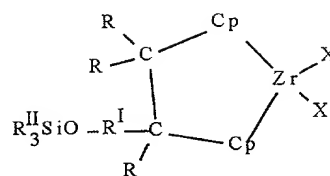
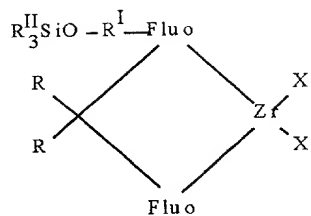
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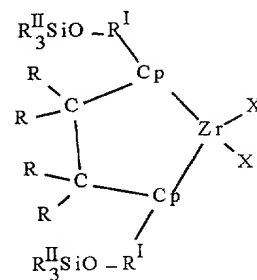
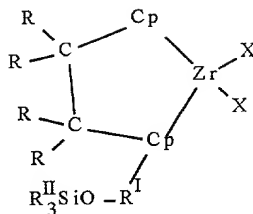
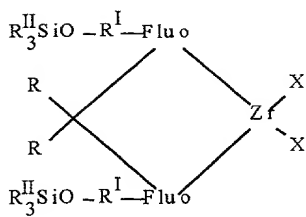
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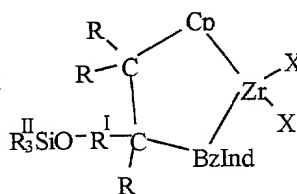
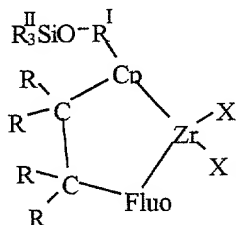
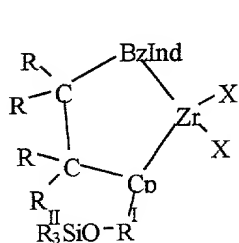
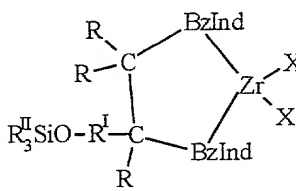
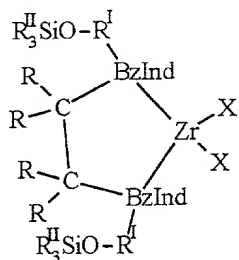
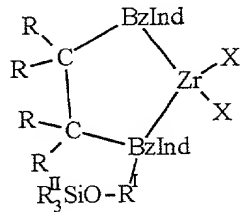
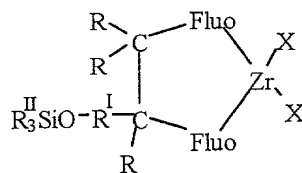
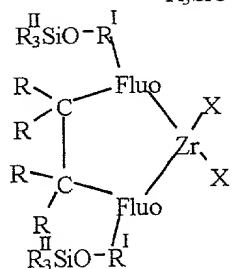
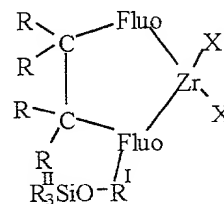
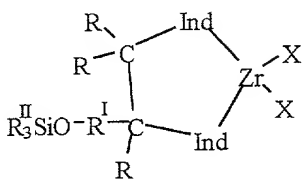
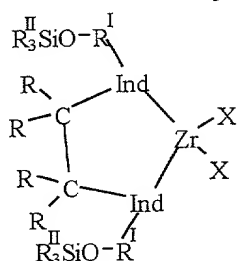
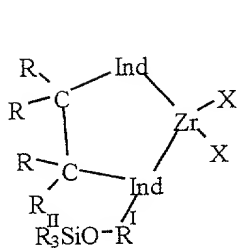
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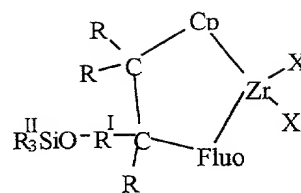
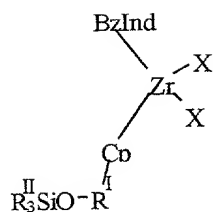
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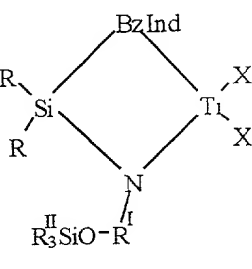
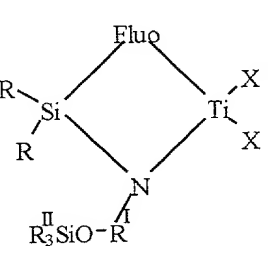
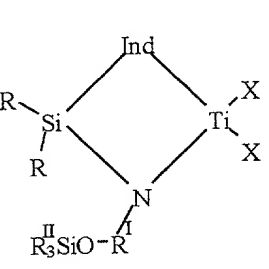
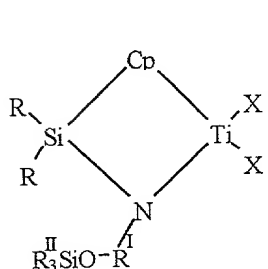
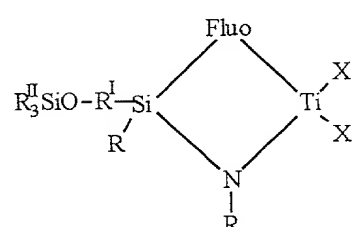
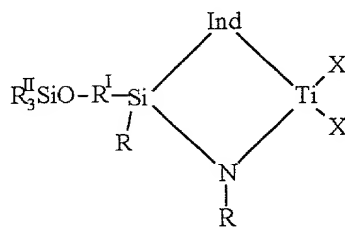
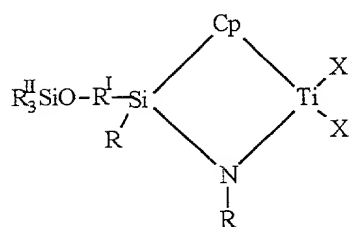
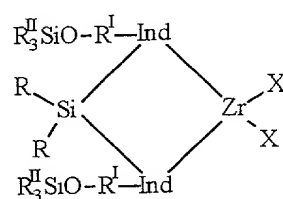
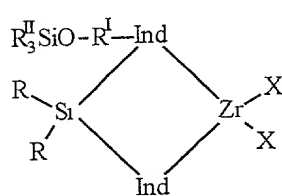
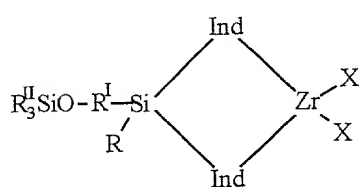
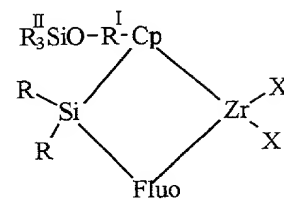
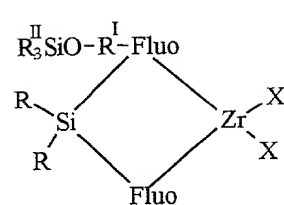
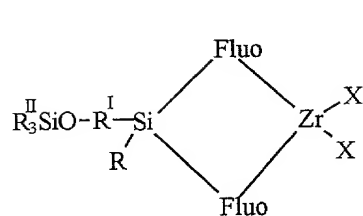
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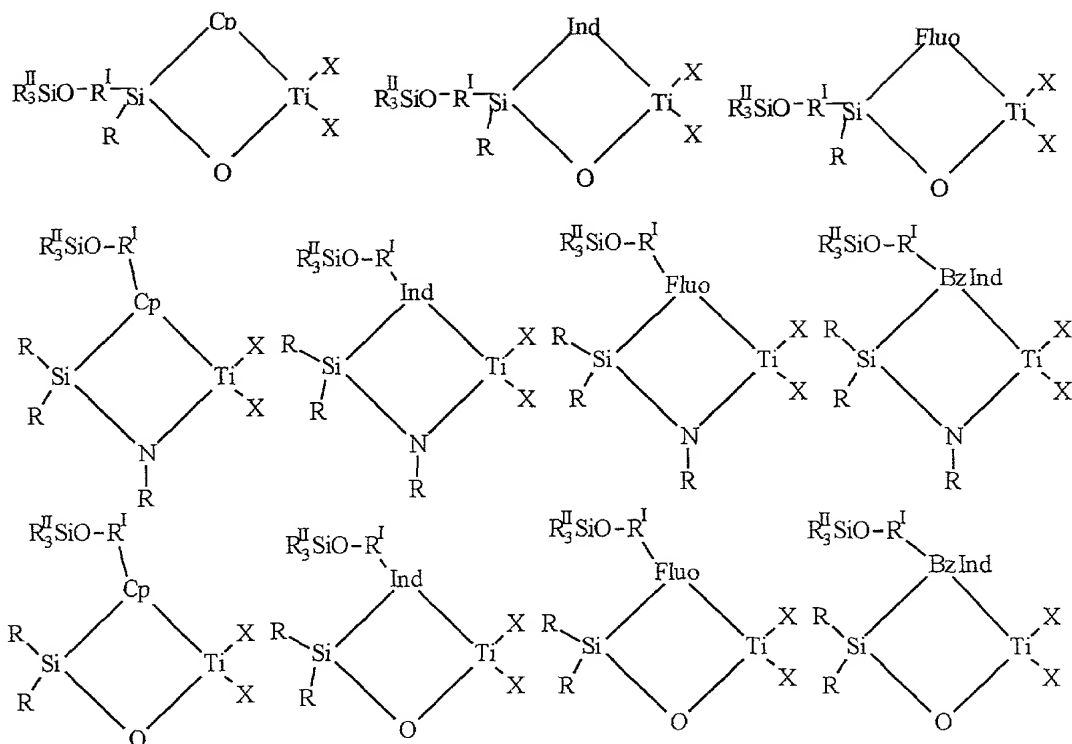


20



5





Wherein Cp, Ind, BzInd and Fluo indicate respectively a cyclopentadienyl, indenyl,  
 5 benzoindenyl and fluorenyl ring optionally substituted by C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl; the maximum number of substituents depends on the amount of hydrogen which can be substituted; R, R<sup>I</sup>, R<sup>II</sup> and X have the above indicated meaning.

Preferred compounds for use in the present invention are the following:

- 10 bis(trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(indenyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;
- 15 (trimethylsiloxyethyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;  
 [1-(2-trimethylsiloxyethyl)indenyl] (cyclopentadienyl) zirconium dichloride  
 [1-(2-methylsiloxyethyl)indenyl] (pentamethyl cyclopentadienyl) zirconium dichloride
- 20 bis(trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxypropyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxypropyl-cyclopentadienyl)(indenyl) zirconium dichloride;

(trimethylsiloxypropyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 (trimethylsiloxypropyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;  
 (trimethylsiloxypropyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;  
 (trimethylsiloxypropyl-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;  
 5 [1-(3-trimethylsiloxypropyl)indenyl](cyclopentadienyl) zirconium dichloride;

bis(trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxy-methoxy-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride ;  
 (trimethylsiloxy-methoxy-cyclopentadienyl)(indenyl) zirconium dichloride;  
 10 (trimethylsiloxy-methoxy-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 (trimethylsiloxy-methoxy-cyclopentadienyl)(fluorenyl) zirconium dichloride;  
 (trimethylsiloxy-methoxy-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;  
 (trimethylsiloxy-methoxy-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium  
 dichloride;

15 bis(trimethylsiloxy-ethoxy-cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxy-ethoxy-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride ;  
 (trimethylsiloxy-ethoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 (trimethylsiloxy-ethoxy-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 20 (trimethylsiloxy-ethoxy-cyclopentadienyl)(fluorenyl) zirconium dichloride;  
 (trimethylsiloxy-ethoxy-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;  
 (trimethylsiloxy-ethoxy-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

bis(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl) zirconium dichloride;  
 25 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxy-propyl-(dimethyl)silyl-cyclopentadienyl)(cyclopentadienyl) zirconium  
 dichloride;  
 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(indenyl) zirconium dichloride;  
 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 30 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;  
 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium  
 dichloride;  
 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(pentamethylcyclopentadienyl)  
 zirconium dichloride;

35 bis(trimethylsiloxy-(dimethyl)silyl-cyclopentadienyl) zirconium dichloride;

(trimethylsiloxy-(dimethyl)silyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiylbis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiylbis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl) (ciclopentadienyl)zirconium

5 dichloride;

dimethylsilandiyl(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(ciclopentadienyl) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium

10 dichloride;

dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;

dimethylsilandiyl(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

15 dimethylsilandiyl(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

dimethylsilandiyl(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methylbenzoindenyl))

20 zirconium dichloride;

dimethylsilandiylbis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;

dimethylsilandiylbis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;

dimethylsilandiyl(3-trimethylsiloxypropyl-cyclopentadienyl) (ciclopentadienyl) zirconium  
 dichloride;

25 dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl)) (ciclopentadienyl) zirconium dichloride;

dimethylsilandiyl(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiyl(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiyl(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;

30 dimethylsilandiyl(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;

dimethylsilandiyl(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium

35 dichloride;

dimethylsilyl(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methylbenzoindenyl))  
zirconium dichloride;

dimethylsilandiylbis(2-trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;  
dimethylsilandiylbis(3-trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;  
dimethylsilandiyl(2-trimethylsiloxy-methoxy-cyclopentadienyl)(1-indenyl) zirconium  
dichloride;

dimethylsilandiyl(2-trimethylsiloxy-methoxy-cyclopentadienyl)(1-(2-methyl-indenyl))  
zirconium dichloride;

15      zirconium dichloride:

dimethylsilyl(3-trimethylsiloxy-methoxy-cyclopentadienyl)(9-fluorenyl) zirconium  
dichloride:

dimethylsilandiyl(3-trimethylsiloxy-methoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl))  
zirconium dichloride:

30 dichloride;

dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

35 dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium

dimethylsilandiyl(3-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride:

- 5 dimethylsilandiylbis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium  
dichloride;  
dimethylsilandiylbis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium  
dichloride;  
dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl)  
10 zirconium dichloride;  
dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl)  
zirconium dichloride;  
dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-  
indenyl)) zirconium dichloride;  
15 dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-  
indenyl)) zirconium dichloride;  
dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl)  
zirconium dichloride;  
dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl)  
20 zirconium dichloride;  
dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-  
fluorenyl)) zirconium dichloride;  
dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-  
fluorenyl)) zirconium dichloride;  
25 dimethylsilandiyl(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium  
dichloride;  
dimethylsilandiyl(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-(2-  
methylbenzoindenyl)) zirconium dichloride;  
dimethylsilandiylbis(1-(3-trimethylsiloxy-(dimethyl)silyl)-indenyl) zirconium dichloride;  
30 dimethylsilandiyl(1-(3-trimethylsiloxy-(dimethyl)silyl)-indenyl) (1-indenyl)zirconium dichloride;  
  
isopropylidenebis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
isopropylidenebis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
35 isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;



- isopropylidene(1-(3-trimethylsiloxyethyl-indenyl)(cyclopentadienyl) zirconium dichloride;  
 isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 5 dichloride;  
 isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 10 isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium  
 dichloride;  
 15 isopropylidenebis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
 isopropylidenebis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
 isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxypropyl-indenyl)(cyclopentadienyl) zirconium dichloride;  
 20 isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 25 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 30 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium  
 dichloride;  
 isopropylidenebis(2-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
 isopropylidenebis(3-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
 isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 35 isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

5 isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl))

10 zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;

15 isopropylidenebis(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

20 isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium

25 dichloride;

isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

30 isopropylidenebis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;

isopropylidenebis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium

35 dichloride;

isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

5 isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl)

10 zirconium dichloride;

isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

15 isopropylidene(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

isopropylidene(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;

20 ethylidenebis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;

ethylidenebis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;

ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;

ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

25 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(cyclopentadienyl) zirconium dichloride;

ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

30 ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium

35 dichloride;

ethylidenebis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;  
ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
5 ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(cyclopentadienyl) zirconium dichloride;  
ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
10 dichloride;  
ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
15 ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
  
ethylidenebis(2-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
20 ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
25 dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
30 ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
  
ethylidenebis(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
35 ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;

ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;

5 ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;

ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

10 ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

ethylidenebis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;

ethylidenebis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;

15 ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium  
dichloride;

ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium  
dichloride;

20 ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl))  
zirconium dichloride;

ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl))  
zirconium dichloride;

ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium  
dichloride;

25 ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium  
dichloride;

ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl))  
zirconium dichloride;

ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl))

30 zirconium dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

35 dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

5 dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
10 dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;  
15 dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;  
dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

20 dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;  
dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;  
dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
25 dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
30 dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

35 dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

5 dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;

10 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;

15 dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

20 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;

25 dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium  
 dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium  
 dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl))  
 zirconium dichloride;

30 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl))  
 zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium  
 dichloride;

35 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium  
 dichloride;

dimethylsilyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl))  
zirconium dichloride;

dimethylsilyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl))  
zirconium dichloride;

5

isopropylidenebis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

isopropylidenebis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

10 isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium

15 dichloride;

isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

isopropylidenebis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

20 isopropylidenebis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;

25 isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium

30 dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

isopropylidenebis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

35 isopropylidenebis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;



isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;

- 5 isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 10 dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

isopropylidenebis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;

- 15 isopropylidenebis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 20 isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 25 dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;

isopropylidenebis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;

- 30 isopropylidenebis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium  
 dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium  
 dichloride;  
 35 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl))

zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl))

zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium

5 dichloride;

isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium

dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl))

zirconium dichloride;

10 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl))

zirconium dichloride;

ethylidenebis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

ethylidenebis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

15 ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

20 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

25 ethylidenebis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

30 ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

dichloride;

ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl) zirconium dichloride;

ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl) zirconium dichloride;

35 dichloride;

- ethylidenebis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
5 ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
10 ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;
- 15 ethylidenebis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
20 ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 25 ethylidenebis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
30 ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium  
35 dichloride;

ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

5 ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilylenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(cyclopentadienyl) zirconium dichloride;

10 dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

15

dimethylsilylenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

20 dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;  
dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilylenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;

25 dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;  
dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium

30 dichloride;

dimethylsilylenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium

35 dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;  
dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

- 5 dimethylsilylenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;  
dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium  
dichloride;  
dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl))  
zirconium dichloride;  
10 dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium  
dichloride;  
dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl))  
zirconium dichloride;  
15 isopropylidenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-fluorenyl) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;  
isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;  
20 isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
isopropylidenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;  
25 isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;  
isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
30 isopropylidenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;  
isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium  
dichloride;  
35 isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;

5 isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium  
10 dichloride;

isopropylidenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium  
dichloride;

15 isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl))  
zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium  
dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl))  
20 zirconium dichloride;

ethylidenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

25 ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;

30 ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

35 ethylidenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;

- 5 ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

- 10 ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;

- 15 ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium

- 20 dichloride;

ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;

- 25 trimethylsiloxyethyl(methyl)silandiylbis(9-fluorenyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

- 30 trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiylbis(1-indenyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;

- 35 trimethylsiloxyethyl(methyl)silandiylbis(1-(2-methylbenzoindenyl)) zirconium dichloride;

- trimethylsiloxypropyl(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxypropyl(methyl)silandiylbis(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 5 dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 trimethylsiloxypropyl(methyl)silandiylbis(1-indenyl) zirconium dichloride;  
 10 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methylbenzoidenyl)) zirconium  
 dichloride;  
  
 trimethylsiloxy-methoxy(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
 15 trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 20 dichloride;  
  
 trimethylsiloxy-ethoxy(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
 25 dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
  
 30 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiylbis(cyclopentadienyl) zirconium  
 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium  
 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl))  
 35 zirconium dichloride;



trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

5

trimethylsiloxy-methoxy(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl))

10

zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

15

trimethylsiloxy-ethoxy-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl))

20

zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

25

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;

30

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

35

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidenebis(1-indenyl) zirconium dichloride;

1-trimethylsiloxyethyl-ethylidenebis(cyclopentadienyl) zirconium dichloride;

1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;

5 1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;

1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;

1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;

10 1-trimethylsiloxyethyl-ethylidenebis(1-indenyl) zirconium dichloride;

1-trimethylsiloxypropyl-ethylidenebis(cyclopentadienyl) zirconium dichloride;

1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;

15 1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;

1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;

1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;

20 1-trimethylsiloxypropyl-ethylidenebis(1-indenyl) zirconium dichloride;

1-trimethylsiloxy-methoxy-ethylidenebis(cyclopentadienyl) zirconium dichloride;

1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;

1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;

25 1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;

1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;

30 1-trimethylsiloxy-ethoxy-ethylidenebis(cyclopentadienyl) zirconium dichloride;

1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;

1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;

1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;

35 1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium

dichloride;

1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidenebis(cyclopentadienyl) zirconium dichloride;

1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium

5 dichloride;

1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl))  
zirconium dichloride

1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl)

zirconium dichloride;

10 1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-  
fluorenyl)) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium

15 dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium

dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

20 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium

dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methylbenzoindenyl) titanium

dichloride;

25 (dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxyethylcyclopentadienyl) titanium

dichloride;

(dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxyethylindenyl) titanium

dichloride;

30 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(cyclopentadienyl) titanium dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(tetramethylcyclopentadienyl) titanium

dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-indenyl) titanium dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(9-fluorenyl) titanium dichloride;

35 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-(2-methylbenzoindenyl) titanium

dichloride;

trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(cylopentadienyl) titanium dichloride;

trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium

5 dichloride;

trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium

dichloride;

trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

10 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium

dichloride;

trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(1-(2-methylbenzoindenyl) titanium

dichloride;

15 (dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxypropylcylopentadienyl) titanium

dichloride;

(dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxypropylindenyl) titanium

dichloride;

20 (dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(cylopentadienyl) titanium

dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(tetramethylcyclopentadienyl) titanium

dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-indenyl) titanium

25 dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(9-fluorenyl) titanium

dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-(2-methylbenzoindenyl) titanium

dichloride;

30

trimethylsiloxy-methoxy (methyl)silandiyl-(tertbutylamido)(cylopentadienyl) titanium

dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl)

titanium dichloride;

35 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(cylopentadienyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(tertbutylamido)-(cylopentadienyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-

(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(cylopentadienyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium

dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;  
trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium  
dichloride;

5 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;  
trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl)  
titanium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(indenyl) titanium dichloride;  
trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-indenyl) titanium

10 dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;  
trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-fluorenyl) titanium  
dichloride;

15 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium  
dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl)  
titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylen(tertbutylamido)(1-indenyl) titanium dichloride;

20 trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(1-(2-methyl-indenyl)) titanium  
dichloride;

trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(9-fluorenyl) titanium dichloride;  
trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(9-(2-methyl-fluorenyl)) titanium  
dichloride;

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trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium  
dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl)  
titanium dichloride;

30 trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(1-indenyl) titanium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(1-(2-methyl-indenyl)) titanium  
dichloride:

trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(9-fluorenyl) titanium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium

35 dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl (methyl) methylene (tertbutylamido) (tetramethylcyclopentadienyl) titanium dichloride;

5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

10 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) zirconium dichloride;

15 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;

20 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methylbenzoindenyl)) zirconium dichloride;

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(dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxyethylcyclopentadienyl) zirconium dichloride;

(dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxyethylindenyl) zirconium dichloride;

30

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(cyclopentadienyl) zirconium dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(tetramethylcyclopentadienyl) zirconium dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-indenyl) zirconium dichloride;

35 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(cyclopentadienyl) zirconium dichloride;

trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;

10 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(1-(2-methylbenzoindenyl) zirconium dichloride;

(dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxypopylindenyl) zirconium  
dichloride;

25 (dimethyl)silandiyl-(3-trimethylsiloxypopylamido)(1-indenyl) zirconium  
dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-methoxy (methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) zirconium  
dichloride:

35 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl)  
zirconium dichloride;



trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) zirconium  
dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;

15 trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-  
(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;

25 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl))  
zirconium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl))  
zirconium dichloride:

35 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-indenyl) zirconium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

5

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl)

10 zirconium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(indenyl) zirconium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-indenyl) zirconium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;

15 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-fluorenyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;

20 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylen(tertbutylamido)(1-indenyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;

25 trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(9-fluorenyl) zirconium dichloride;

trimethylsiloxy-methoxy(methyl)methylen(-tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;

30

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(1-indenyl) zirconium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(1-(2-methyl-indenyl)) zirconium

35 dichloride;

trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy-(methyl)methylen(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

- 5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl (methyl) methylene (tertbutylamido) (tetramethylcyclopentadienyl) zirconium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-indenyl) zirconium
- 10 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;
- 15 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 20 trimethylsiloxyethyl(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl) silandiyl-oxo-(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxyethyl(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- 25 trimethylsiloxypropyl(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxypropyl(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;
- 30 trimethylsiloxypropyl(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- 35 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;

- 5 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
 10 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(cyclopentadienyl) titanium  
 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(tetramethylcyclopentadienyl)  
 15 titanium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium  
 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(fluorenyl) titanium dichloride;  
 20 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(9-methylfluorenyl) titanium  
 dichloride

The metallocene compounds according to the invention can be prepared according to the methods disclosed in EP 839836 which is herewith enclosed by reference.

- 25 Supports useful in the preparation of the heterogeneous catalyst of the invention are inorganic oxides, such as: silica, alumina, silica alumina, aluminium phosphates and mixtures thereof, which result in supported catalysts with contents in transition metal between 0.01 and 3% by weight, preferably between 0.1 and 1%.

The inorganic oxide, before treatment with the metallocene, is treated in such a way that  
 30 it has deposited on its surface an alumoxane. Alumoxanes suitable for the preparation of the support are those represented by the formulas:



- 35 wherein R is alkyl or aryl group containing from 1 to 20 carbon atoms; n ranges from 1 to

40, preferably from 5 to 20 and m ranges from 3 to 40 preferably from 3 to 20.

Generally, in the preparation of alumoxane from, for example, aluminum trimethyl and water, a mixture of linear and cyclic compounds are obtained.

The alumoxane can be prepared in a variety of ways. For example, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon.

The treatment of the inorganic porous support can be done according to any method known in the art. For example the alumoxane can be deposited onto the surface of the inorganic support by dissolving the alumoxane into a suitable solvent and adding the inorganic support into the solution, or it can be deposited onto the surface of the porous support by precipitation in the presence of the support.

It is also possible to form the alumoxane directly on the surface of the porous support by reacting an aluminum alkyl with the hydration water present onto the support surface.

A method that can be fit for preparing supported catalysts according to this invention consists in the impregnation, under anhydrous conditions and inert atmosphere, of the solution of any metallocene of formula I, II or III, or a mixture thereof, on the treated supporting material at a proper temperature, preferably between  $-20^{\circ}\text{C}$  and  $90^{\circ}\text{C}$ . The supported catalyst that contains the metallocene can be obtained through filtration and washing with a proper solvent, preferably an aliphatic or aromatic hydrocarbon without polar groups.

Another method that can properly be used consists in depositing the metallocene on the treated support by using a solution of the compound that has to be heterogenized, eliminating the solvent through evaporation and then warming the solid residue at a temperature between  $25$  and  $150^{\circ}\text{C}$ . Besides, the resulting residue, obtained by this process, can be subjected to washing and subsequent filtration.

The supported catalyst does not require addition of alumoxane or ionizing compound to the reactor, but only a certain amount of aluminium trialkyl. This fact constitutes a further clear advantage in view of most polymerization process which require large amounts of aluminoxane.

The most proper polymerization procedure can change according to the chosen type of polymerization process (suspension, gas phase, solution or in bulk).

For the polymerization in suspension, the cocatalyst can previously be mixed with the supported solid catalyst, can be added to the polymerization medium before the supported catalyst, or both operations can be sequentially realized.

The process consists in putting in contact the monomer, or, in certain cases, the

monomer and the comonomer, with a catalytic composition according to the present invention, that includes at least one supported metallocene complex of formula I, II or III, at a proper temperature and pressure.

Examples of olefins that can be polymerized are ethylene, propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene and cyclic olefins.

Suitable olefins that can be used as comonomers to obtain ethylene copolymers are  $\alpha$ -olefins such as propylene, butene, hexene, octene, 4-methyl-1-pentene and cyclic olefins and can be used in proportions from 0,1 to 70% by weight of the total of the monomers. In the case of homopolymerization of ethylene, the density of polymers ranges between 0,950 and 0,965 g/cm<sup>3</sup>; in the case of copolymerization of ethylene, the density is as low as 0,900 g/cm<sup>3</sup>.

To control the molecular weight of the obtained polymers, hydrogen can optionally be used as a chain transfer agent in such proportions that the hydrogen partial pressure, with respect to the olefin one, be from 0,01 to 50%.

In the particular case of the polymerization technique known as suspension process or controlled particle morphology process, the used temperature will be between 30° and 100 °C, the same which is typically used in gas phase.

The used pressure changes according to the polymerization technique; it ranges from atmospheric pressure to 350 MPa.

It has been surprisingly found that the presence of the group -OSiR<sup>II</sup><sub>3</sub> is essential in order to obtain excellent results in term of catalyst activity. If a group Si-Cl is present on the metallocene instead of the group R<sup>I</sup>OSiR<sup>II</sup><sub>3</sub>, the result is clearly inferior. Although it is not yet possible to describe exactly the interaction taking place between alumoxane and trialkylsililoxo group, it seems very clear that it results in a catalyst presenting unique balance between activity of the catalyst and morphology of the obtained polymer, even better than the results disclosed in patent EP 839836.

The activity of the catalyst according to the invention has been measured in homogeneous catalysis and onto silica impregnated with MAO. The same conditions have been used for metallocenes containing a Si-Cl group and for metallocenes which do not contain a functional group which can react with silica. Table I shows that the metallocene according to the invention is slightly less active under homogeneous condition than the corresponding non-functionalized metallocene, but it becomes much more active when supported onto treated silica. The same conclusions apply when comparing the metallocene according to the invention with the metallocene containing a Si-Cl group.

The following examples are described in order to better understand the invention. The materials, the chemical compounds and the conditions used in these examples are illustrative and do not limit the scope of the invention.

## EXAMPLES

### EXAMPLE 1

*Preparation of [(3-trimethylsiloxypropyl)methylsilylen] bis indenyl zirconium dichloride.*

*Preparation of (3-trimethylsiloxypropyl)methyldichlorosilane.*

A 500 ml Schlenk flask equipped with a stir-bar, a reflux condenser and a rubber septum was charged under nitrogen with 103.3g of  $\text{HSiMe}_2\text{Cl}$  and 5 drops of a 0.1M solution of the platinum  $\text{Pt}(0)$  2,4,6,8-tetramethyl -2,4,6,8-tetravinylcyclotetrasiloxane complex (a product sold by Aldrich Chemical Co) at room temperature. To this solution 100 g of  $\text{Me}_3\text{SiO}-\text{CH}_2-\text{CH}=\text{CH}_2$  was added during 30 minutes. After the addition was completed, the reaction mixture was gradually heated at 40 °C and maintained at this temperature under stirring for 2 hours, and finally heated at 60 °C for another 5 hours. The desired product can be isolated by distillation under vacuum (10 mbar) at 75 °C. Yield 84%  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.120 (s, 9H,  $\text{Si}(\text{Me})_3$ ), 0.810 (s, 6H,  $\text{SiMe}$ ), 1.120-1.190 (m,  $\text{CH}_2$ ), 1.695-1.792 (m, 2H,  $\text{CH}_2$ ), 3.597 (t, 2H,  $\text{CH}_2$ ).

*Preparation of (3-trimethylsiloxypropyl)methyl bis indenyl silane.*

A 500 ml Schlenk flask equipped with a stir-bar, and a rubber septum was charged under nitrogen with 200 ml of ethyl ether and 34.8 g freshly distilled indene. To this solution 120 ml 2.5M  $\text{BuLi}$  solution in hexane was slowly added at 0 °C, under stirring. The resulting mixture was stirred for 1 hour at 0°C and subsequently for 2 more hours at room temperature. The obtained red solution is again cooled to 0 °C and a solution of 39.9 g of  $\text{Me}_3\text{SiO}(\text{CH}_2)_3\text{Si}(\text{Me})\text{Cl}_2$  in 100 ml is slowly added (1 hour). After a 2 hours stirring, the temperature is allowed to rise and the reaction mixture is stirred for 6 more hours at room temperature. All the solvents are removed under low pressure, and the residue extracted with 300 ml of hexane and the inorganic salts filtered. All the volatiles were again removed, first under low pressure (10 mbar) and then at 80 °C under higher vacuum (0.01 mbar). The desired product was obtained pure by short path distillation of the residue at 0.001 mbar and 160 °C, as a mixture of rac and meso isomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (mixture of all isomers): (-0.3740) – (-0.138)- 0.087 (s, 3H,  $\text{SiMe}$ ), 0.085- 0.091- 0.095(s, 9H,  $\text{Si}(\text{Me})_3$ ), 0.320- 0.651- 0.950- 1.183- 1.34 (br m 4H  $-\text{CH}_2-\text{CH}_2$ ), 3.280- 3.349- 3.425 (t, 2H,  $\text{CH}_2-\text{O}$ ), 3.651- 3.680

(s, 2H, C<sub>9</sub>H<sub>7</sub>), 6.361- 6.422- 6.610- 6.954 (4H, m, C<sub>9</sub>H<sub>6</sub>), 7.229- 7.310- 7.531 (m, 8H, C<sub>9</sub>H<sub>6</sub>).  
MS: m/z(%)= 404 M<sup>+</sup>(1%); 288.7(31%); 246.7(100%); 230.7(30%); 114.7(17%); 72.8(20%).

*Preparation of [(3-trimethylsiloxypropyl)methylsilylen] bis indenyl zirconium dichloride.*

- 5 A 250 ml Schlenk flask equipped with a stir-bar and a rubber septum was charged under nitrogen with 75 ml of ethyl ether and 9.14 g of Me<sub>3</sub>SiO(CH<sub>2</sub>)<sub>3</sub> Si(Me)(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>. To this solution 17.2 ml of a 2.5 M solution of n-BuLi in hexane was slowly added under stirring at 0°C. After the addition was completed, the reaction mixture was stirred 2 hours at room temperature. The solvent was removed and the residue suspended in 75 ml of toluene.
- 10 The above prepared suspension was added to a suspension of ZrCl<sub>4</sub>.2Et<sub>2</sub>O in 100 ml toluene at 0 °C, and stirred for 1 hour. The temperature was allowed to rise and the reaction mixture stirred for 5 more hours. The final suspension was filtered through Celite™ and the solvent removed under low pressure until an orange red viscous oil was obtained. The addition of hexane yielded a yellow orange solid shown to be the desired product as a
- 15 mixture of rac and meso isomers. The rac isomer can be obtained pure by extraction of the meso isomer from the original mixture with additional hexane.

- <sup>1</sup>H NMR (CDCl<sub>3</sub>) (mixture of all isomers): 0.157 (s, 9H, SiMe<sub>3</sub>), 0.986-1.152-1.400 (s, 3H, Si(Me)), 0.986- 1.652- 1.783- 2.0546 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>), 3.836 (t, 2H, CH<sub>2</sub>-O), 6.131- 6.158
- 20 (2H, m, C<sub>9</sub>H<sub>7</sub>), 6.952- 6.968 (m, 2H, C<sub>9</sub>H<sub>6</sub>), 7.124- 7.413- 7.457- 7.622 (m, 8H, C<sub>9</sub>H<sub>6</sub>).

EXAMPLE 2

*Preparation of [(1,1-dimethyl-1-sila-4-trimethylsiloxybutyl) cyclopentadienyl] cyclopentadienyl zirconium dichloride:*

25

*Preparation of (3-trimethylsiloxypropyl)dimethylchlorosilane.*

- A 500 ml Schlenk flask equipped with a stir-bar, a reflux condenser and a rubber septum was charged under nitrogen with 94.6 g of HSiMe<sub>2</sub>Cl and 5 drops of a 0.1 M solution of the platinum complex Pt(0) 2,4,6,8-tetramethyl -2,4,6,8-tetravinylcyclotetrasiloxane complex (a
- 30 product sold by Aldrich Chemical Co) at room temperature. To this solution 131 g of Me<sub>3</sub>SiO-CH<sub>2</sub>-CH=CH<sub>2</sub> was added during 30 minutes. After the addition the reaction mixture was gradually heated at 40 °C and maintained at this temperature under stirring for 2 hours, and finally heated at 60 °C for another 5 hours. The desired product can be isolated by distillation under vacuum (25 mbar) at 84 °C. Yield 80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.125 (s, 9H,
- 35 SiMe<sub>3</sub>), 0.413 (s, 6H, SiMe<sub>2</sub>), 0.798-0.890 (m, 2H, CH<sub>2</sub>), 1.595-1.720 (m, 2H, CH<sub>2</sub>), 3.585 (t, 2H, CH<sub>2</sub>).



*Preparation of (1,1-dimethyl-1-sila-4-trimethylsiloxybutyl)cyclopentadiene.*

A 1L Schlenk flask equipped with a stir-bar and a rubber septum was charged under nitrogen with 89 g (0.396 mol) of  $\text{Me}_3\text{SiO}(\text{CH}_2)_3\text{Si}(\text{Me})_2\text{Cl}$  and 200 ml of dry hexane. To this solution 250 ml of a solution of THF containing 0.396 mol of  $\text{C}_5\text{H}_5\text{Na}$  was added under stirring at 0 °C. After the addition the reaction mixture was maintained at this temperature for 1 hour. The temperature was allowed to raise to 23°C and the mixture was stirred for 8 more hours. The final suspension was filtered, subsequently, the volatiles were removed at reduced pressure. The product was isolated from the residue by distillation at 65-68 °C and 1 mbar as a mixture of double bond isomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): -0.03 (s, 6H,  $\text{Si}(\text{Me})_2$ ), 0.2 (s, 9H,  $\text{Si}(\text{Me})_3$ ), 0.52-0.68 (m, 2H,  $\text{CH}_2$ ), 1.59 (m, 2H,  $\text{CH}_2$ ), 3.45 br (1H  $\text{C}_5\text{H}_4$ ), 3.55 (t, 2H,  $\text{CH}_2\text{-O}$ ), 6.45-6.7 (m, 4H,  $\text{C}_5\text{H}_4$ ).

*Preparation of [(1,1-dimethyl-1-sila-4-trimethylsiloxybutyl)cyclopentadienyl] cyclopenta-dienyl zirconium dichloride.*

A 250 ml Schlenk flask equipped with a stir-bar and a rubber septum was charged under nitrogen with 14 g (0.0396 mol) of  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2 \cdot \text{DME}$  and 100 ml of dry hexane. To this solution 0.0396 mol of  $\text{Me}_3\text{SiO}(\text{CH}_2)_3\text{Si}(\text{Me})_2\text{C}_5\text{H}_4\text{K}$  in 50 ml THF was slowly added at 0 °C, under stirring. The resulting mixture was stirred for 1 hour at 0°C and subsequently for 6 more hours at room temperature. All the solvents were removed under reduced pressure and the solid residue was extracted with hexane and filtered. The solution was again partially evaporated and cooled at -20 °C to give white crystals (Yield 45 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.125 (s, 9H,  $\text{Si}(\text{Me})_3$ ), 0.333 (s, 6H,  $\text{Si}(\text{Me})_2$ ), 0.688-0.722 (m, 2H,  $\text{CH}_2$ ), 1.504-1.538 (m, 2H,  $\text{CH}_2$ ), 3.520 (t, 2H,  $\text{CH}_2$ ), 6.479 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.570 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.725 (m, 2H,  $\text{C}_5\text{H}_4$ ).

### EXAMPLE 3

*Preparation of [1-(3-trimethylsiloxypropyl)indenyl] cyclopentadienyl zirconium dichloride.*

*Preparation of [3-(3 trimethylsiloxypropyl)indene].*

A solution of 25.3 g (230 mmol) of LiInd in 250 ml of THF was slowly added to a solution of 48.5 g (230 mmol) of 3-bromo-1-trimethylsiloxypropane, prepared according to EP 0 839 836, in 250 ml of THF at room temperature. A red solution was immediately formed. The mixture was stirred at room temperature for 12 h and then the solvent was removed under

vacuum, the residue was treated with hexane and the supernatant solution was filtered. The removal of the hexane led to a green oil. This oil was distilled in order to obtain a pale yellow oil. ( $T_b$ : 89-91°C, 1 mm Hg). (21.5 g, 87.4 mmol, yield: 38%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.52 (m, 1H); 7.45 (m, 1H); 7.36 (m, 1H); 7.24 (m, 1H); 6.28 (m, 1H); 3.74 (m, 2H); 3.39 (m, 2H); 2.65 (m, 2H); 1.99 (m, 2H); 0.20 (s, 9H).

*Preparation of lithium [1-(3-trimethylsiloxypropyl)indenide].*

To 1.5 g (6.1 mmol) of [3-(3-trimethylsiloxypropyl)indene] in ether at  $-78^\circ\text{C}$ , 2.44 ml (6.1 mmol) of a 2.5 M butyllithium solution in hexane was added. The immediate formation of a white solid was observed. The mixture was maintained under stirring for 2 h. Then, the solvent was removed under vacuum and the residue was washed twice with 25 ml of hexane to give a brown solid. (1.3 g, 5.2 mmol, yield 85%).

*Preparation of [1-(3-trimethylsiloxypropyl)indenyl] cyclopentadienyl zirconium dichloride.*

To a suspension of 1.0 g (4 mmol) of cyclopentadienyl zirconium trichloride in ether at  $0^\circ\text{C}$ , a suspension of 1.0 g (4 mmol) of lithium [1-(3-trimethylsiloxypropyl)indenide] in ether was added. The formation of a yellowish solid was observed immediately. The mixture was stirred for 12 h, then the supernatant solution was filtered and the volatiles were removed under vacuum to give a yellow oily-solid. This solid was washed with hexane to give a yellow powder, which was characterized as [1-(3-trimethylsiloxypropyl)indenyl] cyclopentadienyl zirconium dichloride (0.85 g, 1.8 mmol, yield: 45%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.67 (m, 2H); 7.30 (m, 2H); 6.70 (m, 1H); 6.45 (m, 1H); 6.13 (s, 5H); 3.65 (m, 2H); 3.04 (dm, 2H); 1.92 (m, 2H); 0.17 (s, 9H).

EXAMPLE 4

*Preparation of dimethylsilylen [3-(2-trimethylsiloxyethyl)cyclopentadienyl] indenyl zirconium dichloride.*

*Preparation of (2-trimethylsiloxyethylcyclopentadienyl) indenyl dimethyl silane.*

To a suspension of 0.63 g (26.3 mmol) of HNa in THF at  $-78^\circ\text{C}$ , a solution of 6.3 g (26.3 mmol) of cyclopentadienylindenyl dimethylsilane in THF was added. Immediately a purple solution was formed. Then, the volatiles were removed and the residue was washed with hexane to give a pink solid. The solid was solved again in THF and a solution of 5.2 g (26.3 mmol) of 2-bromo-1-trimethylsiloxyethane in THF was added at room temperature. A white suspension was formed immediately. The mixture was stirred for 12 h, and then the

solvents were removed and the residue was treated with hexane and the supernatant solution was filtered. The removal of the hexane led to a brown oil. This oil was distilled in order to obtain a yellow-orange oil, which was characterized as a mixture of position isomers of (2-trimethylsiloxyethylindenyl) cyclopentadienyl dimethyl silane. ( $T_b$ : 170-175°C; 1 mm Hg), (3.9 g, 11 mmol, yield: 42%).  $^1\text{H}$ -RMN( $\text{CDCl}_3$ ): 7.54-7.42 (m, 2H); 7.31-7.12 (m, 2H); 6.95 (m, 1H); 6.91 (m, 1H); 6.72 (m, 1H); 6.61 (m, 1H); 6.60-6.42 (m, 3H); 3.78 (m, 2H); 3.62 (m, 1H); 3.42 (m, 2H); 2.62 (m, 2H); 0.17 (m, 15 H).

*Preparation of dimethylsilylen [3-(2-trimethylsiloxyethyl)cyclopentadienyl] indenyl zirconium dichloride.*

To a solution of 1.4 g (35 mmol) of HK in THF at room temperature, a solution of 6.2 g (17.5 mmol) of (2-trimethylsiloxyethylindenyl) cyclopentadienyl dimethyl silane in THF is added. Immediately, a purple solution was formed. Then, the solution was added to a suspension of 4.1 g (17.5 mmol) of zirconium tetrachloride in toluene at  $-78^\circ\text{C}$ . The formation of a yellow suspension was observed. The mixture was stirred for 12 h and then the solvents were evaporated, the residue was treated with hexane and the supernatant solution was filtered and stored at  $-35^\circ\text{C}$ . A yellow microcrystalline solid was obtained, which was characterized as a mixture in a ratio 50:50 of two stereoisomers. (5.8 g, 11.3 mmol, yield: 65%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 7.75 (m, 2H, Isomer a and b); 7.52 (m, 1H, Isomer a); 7.41 (m, 1H, Isomer b); 7.12 (m, 4H, Isomer a and b); 6.51 (m, 1H, Isomer b); 6.48 (m, 1H, Isomer a); 6.22 (m, 1H, Isomer a); 6.11 (m, 1H, Isomer b); 5.90 (m, 1H, Isomer a); 5.83 (m, 1H, Isomer b); 5.57 (m, 1H, Isomer b); 5.54 (m, 1H, Isomer a); 3.78 (m, 2H, Isomer b); 3.67 (m, 2H, Isomer a); 2.88 (m, 2H, Isomer b); 2.70 (dm, 2H, Isomer a); 1.03 (s, 3H, Isomer b); 1.02 (s, 3H, Isomer a); 0.82 (s, 3H, Isomer a); 0.80 (s, 3H, Isomer b); 0.10 (s, 9H, Isomer b); 0.08 (s, 9H, Isomer a);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 141.0, 138.7, 135.1, 135.0, 127.8, 127.2, 126.3, 126.1, 125.8, 124.1, 123.7, 123.6, 119.2, 119.1, 117.6, 117.4, 116.2, 115.7, 115.6, 112.3, 112.2, 105.5, 104.7, 89.8, 89.7, 62.3, 62.2, 33.3, 33.2, -0.51, -2.34, -2.35, -4.62, -4.63.

### EXAMPLE 5

*Preparation of dimethylsilylen [3-(2-trimethylsiloxyethyl)cyclopentadienyl] cyclopentadienyl zirconium dichloride.*

*Preparation of (2-trimethylsiloxyethylcyclopentadienyl) cyclopentadienyl dimethyl silane.*

A solution of 11.5 g (61 mmol) of biscyclopentadienyldimethylsilane in THF was added to a suspension of 1.3 g (55 mmol) of HK in THF at  $-78^\circ\text{C}$ . A purple solution was immediately

formed. Then, the volatiles were removed and the residue was washed with hexane to give a pink solid. The solid was solved again in THF and a solution of 10.8 g (55 mmol) of 2-bromo-1-trimethylsiloxyethane in THF was added at room temperature. A pink suspension was immediately formed. The mixture was stirred for 12 h, and then the solvents were removed, the residue was treated with hexane and the supernatant solution was filtered. The removal of the hexane led to a reddish oil. This oil was distilled in order to obtain a yellow oil, which was characterized as a mixture of position isomers of (2-trimethylsiloxyethylcyclopentadienyl) dimethyl cyclopentadienyl silane ( $T_b$ : 135-140°C; 1 mm Hg), (8.7 g, 28.6 mmol, yield: 52%).  $^1\text{H-NMR}(\text{CDCl}_3)$ : 6.82-6.40 (m, 7H); 3.82 (m, 2H); 3.10 (m, 2H); 2.73 (m, 2H); 0.20 (s, 15 H).

*Preparation of dimethylsilylen [3-(2-trimethylsiloxyethyl)cyclopentadienyl] cyclopentadienyl zirconium dichloride.*

4.24 ml (10.6 mmol) of a 2.5 M butyllithium solution in hexane was added to a solution of 1.6 g (5.3 mmol) of (2-trimethylsiloxyethylcyclopentadienyl) cyclopentadienyl dimethyl silane in ether at room temperature. The immediate formation of a white solid was observed. After 2 h the mixture was added to a suspension of 1.2 g (5.3 mmol) of zirconium tetrachloride in toluene at  $-78^\circ\text{C}$ . The formation of a yellow suspension was observed. The mixture was stirred for 12 h and then the solvents were evaporated, the residue was treated with hexane and the supernatant solution was filtered. The removal of the hexane led to a green solid, which was recrystallized in hexane at  $-35^\circ\text{C}$  to give a green powder, which is characterized as dimethylsilylen [3-(2-trimethylsiloxyethyl)cyclopentadienyl] cyclopentadienyl zirconium dichloride (0.4 g, 0.86 mmol, yield: 16%).  $^1\text{H-NMR}(\text{CDCl}_3)$ : 7.05 (m, 1H); 6.96 (m, 1H); 6.67 (m, 1H); 5.98 (m, 1H); 5.92 (m, 1H); 5.86 (m, 1H); 5.60 (m, 1H) 3.80 (m, 2H); 2.88 (m, 2H); 0.72 (s, 3H); 0.77 (s, 3H); 0.10 (s, 9 H).  $^{13}\text{C-NMR}(\text{CDCl}_3)$ : 138.9, 127.3, 126.7, 126.6, 114.5, 113.5, 113.3, 112.9, 107.1, 107.0, 62.6, 34.4, 1.1, -3.5, -3.6.

**EXAMPLE 6**

*Preparation of [1-(2-trimethylsiloxyethyl)indenyl] cyclopentadienyl zirconium dichloride.*

*Preparation of [3-(2-trimethylsiloxyethyl)indene].*

A solution of 43.1 g (392 mmol) of LiInd in 250 ml of THF was slowly added to a solution of 82.7 g (392 mmol) of 2-bromo-1-trimethylsiloxyethane, prepared according to EP 0 839 836, in 250 ml of THF at  $0^\circ\text{C}$ . An orange solution is immediately formed. The mixture was stirred at room temperature for 12 h and then the solvent was removed under vacuum, the

residue was treated with hexane and the supernatant solution was filtered. The removal of the hexane led to a dark brown oil. This oil was distilled in order to obtain a pale yellow oil. ( $T_b$ : 84-86°C, 1 mm Hg). (41.8 g, 180 mmol, yield: 46%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.52 (m, 1H); 7.45 (m, 1H); 7.36 (m, 1H); 7.25 (m, 1H); 6.31 (m, 1H); 3.96 (m, 2H); 3.40 (m, 2H); 2.90 (m, 2H); 0.19 (s, 9H).

*Preparation of lithium [1-(2-trimethylsiloxyethyl)indenide].*

10.3 ml (16.4 mmol) of a 1.6 M butyllithium solution in hexane was added to 3.8 g (16.4 mmol) of [3-(2-trimethylsiloxyethyl)indene] in ether at  $-78^\circ\text{C}$ . The immediate formation of a white solid was observed. The mixture was maintained under stirring for 2 h. Then the solvent was removed under vacuum and the residue was washed twice with 25 ml of hexane to give a white solid. (3.6 g, 15 mmol, yield: 91.5%).

*Preparation of [1-(2-trimethylsiloxyethyl)indenyl] cyclopentadienyl zirconium dichloride.*

15 A suspension of 3.9 g (16.4 mmol) of lithium [1-(2-trimethylsiloxyethyl)indenide] in ether was added to a suspension of 5.8 g (16.4 mmol) of cyclopentadienyl zirconium trichloride complex with dimethoxyethane in 100 ml of ether at  $0^\circ\text{C}$ . The formation of a yellowish solid was immediately observed. The mixture was stirred for 12 h, then the supernatant solution was filtered and the volatiles were removed under vacuum to give a yellow oily-solid. This solid was washed with hexane to give a yellow powder, which was characterized as [1-(2-trimethylsiloxyethyl)indenyl] cyclopentadienyl zirconium dichloride (3.3 g, 7.2 mmol, yield: 44%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.65 (m, 2H); 7.29 (m, 2H); 6.67 (m, 1H); 6.46 (m, 1H); 6.12 (s, 5H); 3.87 (m, 2H); 3.20 (dm, 2H); 0.05 (s, 9H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 127.2, 125.3, 125.2, 125.0, 124.9, 124.1, 116.1, 97.8, 97.7, 62.3, 31.3, -0.8.

EXAMPLE 7

*Preparation of [1-(2-trimethylsiloxyethyl)indenyl] pentamethylcyclopentadienyl zirconium dichloride.*

30 *Preparation of [1-(2-trimethylsiloxyethyl)indenyl] pentamethylcyclopentadienyl zirconium dichloride.*

A suspension of 1.5 g (6.5 mmol) of lithium [1-(2-trimethylsiloxyethyl)indenide] in ether was added to a suspension of 2.2 g (6.5 mmol) of pentamethylcyclopentadienyl zirconium trichloride in 100 ml of ether at  $0^\circ\text{C}$ . After 30 minutes, the formation of a white solid was observed. The mixture was stirred for 12 h, then the supernatant solution was filtered and

the volatiles were removed under vacuum to give a yellow oily-solid. This solid was recrystallized in hexane to give a microcrystalline yellow solid, which was characterized as [1-(2-trimethylsiloxyethyl)indenyl] pentamethylcyclopentadienyl zirconium dichloride (1.7 g, 3.2 mmol, yield: 49%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.65 (m, 1H); 7.33 (m, 1H); 7.25 (m, 2H); 6.08 (m, 1H); 5.92 (m, 1H); 3.72 (dm, 2H); 3.28 (m, 1H); 2.72 (m, 1H); 2.04 (s, 15H); 0.03 (s, 9H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 131.4; 127.1; 126.7; 125.2; 125.1; 124.2; 123.5; 122.6; 116.1; 97.0; 62.6; 32.1; 12.5; -0.6.

## PREPARATION OF SUPPORTED FUNCTIONALIZED METALLOCENES

### EXAMPLE 8

*Heterogenization of (3-trimethylsiloxypropylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (3-trimethylsiloxypropylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,29 % and 19,4 % by weight respectively.

### COMPARATIVE EXAMPLE 9

*Heterogenization of (chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,40 % and 20,7 % by weight respectively.

COMPARATIVE EXAMPLE 10

*Heterogenization of (chloromethylsilandiyl)bis(cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (chloromethylsilandiyl)bis(cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,36 % and 18,1 % by weight respectively.

EXAMPLE 11

*Heterogenization of (3-trimethylsiloxypropyl)methylsilylen]bis(1-indenyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3 g of silica modified with MAO commercialized by Witco with a 23% by weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of [(3-trimethylsiloxypropyl)methylsilylen]bis(1-indenyl) zirconium dichloride (0,2 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene up to a total volume of 250 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,41 % and 22 % by weight respectively.

EXAMPLE 12

*Heterogenization of [(1,1-dimethyl-1-sila-4-trimethylsiloxybutyl)-cyclopentadienyl] cyclopentadienyl zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3 g of silica modified with MAO commercialized by Witco with a 23% by weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of [(1,1-dimethyl-1-sila-4-trimethylsiloxybutyl)-cyclopentadienyl] cyclopentadienyl zirconium dichloride (0,33 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions

of toluene up to a total volume of 250 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,99 % and 22,4 % by weight respectively.

### 5      EXAMPLE 13

*Heterogenization of [1-(3-trimethylsilosypropyl)indenyl](cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3 g of silica modified with MAO commercialized by Witco with a 23% by weight of Al and it was added 120 ml of toluene.  
 10 Then, it was added a solution in toluene of [1-(3-trimethylsilosypropyl)indenyl](cyclopentadienyl) zirconium dichloride (0,140 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene up to a total volume of 250 ml. The solid was finally dried under vacuum  
 15 for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,59 % and 27 % by weight respectively.

### EXAMPLE 14

*Heterogenization of dimethylsilylen(trimethylsiloxyethyl-3cyclopentadienyl)(1-indenyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3 g of silica modified with MAO commercialized by Witco with a 24,7% by weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of dimethylsilylen(trimethylsiloxyethyl-3-cyclopentadienyl)(1-indenyl) zirconium dichloride (0,152 mmol of Zr). The reaction mixture  
 25 was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70°C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,35 % and 20 % by weight respectively.

### EXAMPLE 15

*Heterogenization of dimethylsilylen(trimethylsiloxyethyl-3cyclopentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3,2 g of silica modified with MAO  
 35 commercialized by Witco with a 24,7% by weight of Al and it was added 120 ml of toluene.



Then, it was added a solution in toluene of *dimethylsilylen(trimethylsiloxyethyl-3 cyclopentadienyl)(cyclopentadienyl) zirconium dichloride* (0,096 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,24 % and 23 % by weight respectively.

#### EXAMPLE 16

*Heterogenization of [1-(2-trimethylsiloxyethyl)Indenyl](cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighted 3,7 g of silica modified with MAO commercialized by Witco with a 24,7% by weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of [1-(2-trimethylsiloxyethyl)Indenyl](cyclopentadienyl) zirconium dichloride (0,111 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,23 % and 23 % by weight respectively.

#### PREPARATION OF SUPPORTED NON-FUNCTIONALIZED METALLOCENES

##### COMPARATIVE EXAMPLE 17

*Heterogenization of biscyclopentadienyl zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of biscyclopentadienyl zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,36 % and 18,4 % by weight respectively.

EXAMPLE 18

*Heterogenization of (trimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (trimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,4 % and 21,2 % by weight respectively.

EXAMPLE 19

*Heterogenization of (dimethylsilyl)bis(cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (dimethylsilyl)bis(cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,37 % and 20,8 % by weight respectively.

POLYMERIZATION WITH FUNCTIONALIZED SOLUBLE CATALYSTSCOMPARATIVE EXAMPLE 20

*Copolymerization of ethylene/1-hexene*

The reactions of copolymerization of ethylene/1-hexene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to 4 atm.

Then, it was added 20 ml of 1-hexene, 2,7 ml of a solution of MAO 10% in toluene

(commercialized by Witco) and finally 0,42 ml of a solution  $4,7 \times 10^{-3}$  M in toluene of (3-trimethylsiloxy propyl cyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,002 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 10,4 g of polyethylene (activity  $5,2 \times 10^6$  g PE/mol M x h x atm) with a Mw of 172.800, MWD of 4 and a comonomer content of 1,77% molar.

#### COMPARATIVE EXAMPLE 21

##### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to 4 atm. Then, it was added 1,1 ml of a solution of MAO 10% in toluene (commercialized by Witco) and 0,28 ml of a solution  $2,8 \times 10^{-3}$  M in toluene of (chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,0008 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 8,1 g of polyethylene (activity  $10,0 \times 10^6$  g PE/mol M x h x atm) with a Mw of 288.300 and MWD 2.2.

#### COMPARATIVE EXAMPLE 22

##### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 21, but it was added 5,3 ml of a solution of MAO 10% in toluene (commercialized by Witco) and 0,93 ml of a solution  $4,3 \times 10^{-3}$  M in toluene of (chloromethylsilyl) bis (cyclopentadienyl) zirconium dichloride (0,004 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 5,1 g of polyethylene (activity  $1,3 \times 10^6$  g PE/mol M x h x atm) with a Mw of 162.000.

#### COMPARATIVE EXAMPLE 23

The polymerization reaction of ethylene was carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to 4 atm. Then, it was added

26,7 ml of a solution of MAO 1,5 M in Toluene, 10 ml of 1-hexene and 5,3 ml of a solution in toluene ( $1,5 \times 10^{-3}$  M) of [1-(2-methylsiloxyethyl) Indenyl] (pentamethyl cyclopentadienyl) zirconium dichloride (0,008 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 7,3 g of polyethylene (activity  $9,2 \times 10^5$  g PE/mol M x h x atm) with an Mw of 215.400 and a comonomer content of 0,7% molar.

## POLYMERIZATION WITH NON-FUNCTIONALIZED SOLUBLE CATALYSTS

### COMPARATIVE EXAMPLE 24

#### *Copolymerization of ethylene/1-hexene*

The reaction of copolymerization of ethylene with 1-hexene was carried out by following the method and the conditions described in example 20, but it was added 2,7 ml of a solution of MAO 10% in toluene commercialized by Witco and finally 0,7 ml of a solution in toluene ( $2,7 \times 10^{-3}$  M) of biscyclopentadienyl zirconium dichloride (0,002 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 16 g of polyethylene (activity  $8,0 \times 10^6$  g PE/mol M x h x atm) with a Mw of 59.300, MWD 2.4 and a comonomer content of 1,08% molar.

### COMPARATIVE EXAMPLE 25

#### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 21, but it was added 1,1 ml of a solution of MAO 10% in toluene (commercialized by Witco) and then 0,3 ml of a solution in toluene ( $3,0 \times 10^{-3}$  M) of (trimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,0008 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 13,5 g of polyethylene (activity  $16,9 \times 10^6$  g PE/mol M x h x atm) with a Mw of 319.200 and MWD 2.3.

### COMPARATIVE EXAMPLE 26

#### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 21, but it was added 5,3 ml of a solution of MAO 10% in toluene commercialized by Witco and finally 0,87 ml of a solution in toluene ( $4,6 \times 10^{-3}$  M) of (dimethylsilandyil)bis(cyclopentadienyl) zirconium dichloride (0,004 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 11,7 g of polyethylene (activity  $2,90 \times 10^6$  g PE/mol M x h x atm) with a Mw of 64.500 and MWD 3.5.

## POLYMERIZATION WITH FUNCTIONALIZED SUPPORTED CATALYSTS

### EXAMPLE 27

#### *Copolymerization of ethylene/1-hexene*

The reactions of copolymerization of ethylene with 1-hexene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to a pressure of 3,5 atm, then it was added 20 ml of 1-hexene, 1,7 ml of a solution of TIBA 1,34 M in heptane and it was finally added, through a overpressure of ethylene of 0,5 atm, 0,179 g (0,0057 mmol of Zr) of the catalyst prepared according to example 8. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 13,8 g of polyethylene (activity  $2,4 \times 10^6$  g PE/mol M x h x atm) with a Mw of 178.600, a MWD of 2,4 and a comonomer content of 2,27% molar.

### EXAMPLE 28

#### *Polymerization of ethylene*

The reactions of polymerization of ethylene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to a pressure of 3,5 atm. Later, it was added 1,7 ml of a solution of TIBA 1,34 M in heptane and it was finally added, through a overpressure of ethylene of 0,5 atm, 0,130 g (0,0057 mmol of Zr) of the catalyst described in example 9. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 6 g of polyethylene (activity  $1,1 \times 10^6$  g PE/mol M x h x atm) with a Mw of 378.500 and MWD 2.6.

EXAMPLE 29*Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 28, but it was added 2,4 ml of a solution of TIBA 1,34 M in heptane and 0,203 g (0,008 mmol of Zr) of the catalyst described in example 10. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,5 g of polyethylene (activity  $0,32 \times 10^6$  g PE/mol M x h x atm) with a Mw of 159.600 and MWD 5.3.

EXAMPLE 30

The reaction of copolymerization of ethylene with 1-hexene was carried out in an autoclave of a capacity of 2 liters, under anhydrous conditions. The reactor, charged with 1 l of dry isobutane, 49,6 ml of 1-hexene and 0,83 ml of a solution of TIBA 0,61 M in heptane, was conditioned at a temperature of 85°C. Later, it was added 0,033 g (0,0015 mmol of Zr) of the catalyst prepared according to example 11 and the reactor was pressurized with ethylene up to a total pressure of 40 atm. The copolymerization reaction was maintained at 85°C and at a pressure of 40 atm for 60 minutes. At the end of the reaction, the reactor was depressurized and it was obtained 255,4 g of polyethylene (activity  $4,3 \times 10^6$  g PE/mol M x h x atm) with a Mw of 311.200, MWD of 7,9, a comonomer content of 1,27% molar (hexene), and 0,17% molar (butene). The powder bulk density was 0,38 g/cc.

EXAMPLE 31

The copolymerization reaction of ethylene/1-hexene was carried out by following the method and the conditions described in example 30, but it was added 141,5 ml of 1-hexene and 7,7 ml of a solution of TIBA 0,61 M in heptane. Later, it was added 0,071 g (0,0077 mmol of Zr) of the catalyst prepared according to example 12 and the reactor was pressurized with ethylene up to a total pressure of 40 atm. The copolymerization reaction was maintained at 85°C and at a pressure of 40 atm for 60 minutes. At the end of the reaction, the reactor was depressurized and it was obtained 181 g of polyethylene (activity  $0,6 \times 10^6$  g PE/mol M x h x atm), with a comonomer content of 1,1% molar and a bulk density of 0,39 g/cc.

EXAMPLE 32

The copolymerization reaction of ethylene/1-hexene was carried out by following the method and the conditions described in example 30, but it was added 141,5 ml of 1-hexene and 0,74 ml of a solution of TIBA 0,61 M in heptane. Later, it was added 0,034 g (0,0022 mmol of Zr) of the catalyst prepared according to example 13 and the reactor was pressurized with ethylene up to a total pressure of 40 atm. The copolymerization reaction was maintained at 85°C and at a pressure of 40 atm for 60 minutes. At the end of the reaction, the reactor was depressurized and it was obtained 95,4 g of polyethylene (activity  $1,1 \times 10^6$  g PE/mol M x h x atm), with a comonomer content of 0,7% molar and a bulk density of 0,37 g/cc.

#### EXAMPLE 33

The polymerization reaction of ethylene was carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 90°C and pressurized with ethylene up to 4 atm. Then, it was added 9,4 ml of a solution of TIBA 0,64 M in heptane, and 0,391 g (0,015 mmol of Zr) of the catalyst prepared according to example 14. The polymerization reaction was maintained at 90°C and a pressure of 4 atm for 30 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 1,6 g of polyethylene (activity  $5,3 \times 10^4$  g PE/mol M x h x atm).

#### EXAMPLE 34

The copolymerization reaction of ethylene/1-hexene was carried out by following the method and the conditions described in example 33, but it was added 9,4 ml of a solution of TIBA 0,64 M, 10 ml of 1-hexene. Then, it was added 0,540 g (0,014 mmol of Zr) of the catalyst prepared according to example 15. The polymerization reaction was maintained at 90°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,9 g of polyethylene (activity  $2,0 \times 10^5$  g PE/mol M x h x atm) with a comonomer content of 2,0% molar.

#### EXAMPLE 35

The copolymerization reaction of ethylene/1-hexene was carried out by following the method and the conditions described in example 33, but it was added 3,6 ml of a solution of TIBA 0,64 M, 10 ml of 1-hexene. Then, it was added 0,226 g (0,0057 mmol of Zr) of the

catalyst prepared according to example 16 The polymerization reaction was maintained at 90°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 1,1 g of polyethylene (activity  $2 \times 10^5$  g PE/mol M x h x atm) with a comonomer content of 1,2% molar.

## POLYMERIZATION WITH NON-FUNCTIONALIZED SUPPORTED CATALYSTS

### EXAMPLE 36

#### *Copolymerization of ethylene/ 1-hexene*

The reaction of copolymerization of ethylene with 1-hexene was carried out by following the method and the conditions described in example 27, but it was added 0,144 g (0,0057 mmol of Zr) of the catalyst described in example 17. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,8 g of polyethylene (activity  $0,5 \times 10^6$  g PE/mol M x h x atm) with a Mw of 157.900, (MWD) of 3,7 and a comonomer content of 1,53% molar.

### COMPARATIVE EXAMPLE 37

#### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 28, but it was added 0,130 g (0,0057 mmol of Zr) of the catalyst described in example 18. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 6,2 g of polyethylene (activity  $1,1 \times 10^6$  g PE/mol M x h x atm) with a Mw of 327.600 and MWD 2.3.

### COMPARATIVE EXAMPLE 38

#### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 28, but it was added 2,4 ml of a solution of TIBA 1,34 M in heptane and 0,179 g (0,008 mmol of Zr) of the catalyst prepared according to example 19.

The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15



minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,4 g of polyethylene (activity  $0,3 \times 10^6$  g PE/mol M x h x atm) with a Mw of 86.900 and MWD 4.7.

## 5 COMPARATIVE EXAMPLE 39

### *Copolymerization of ethylene/1-hexene in Autoclave*

The reaction of copolymerization of ethylene with 1-hexene was carried out in an autoclave of a capacity of 2 liters, under anhydrous conditions. The reactor, charged with 1 l of dry isobutane, 124 ml of 1-hexene and 0,6 ml of a solution of TIBA 1,34 M in heptane, was conditioned at a temperature of 90°C. Later, it was added 0,1 g (0,003 mmol of Zr) of the catalyst prepared according to example 8 and the reactor was pressurized with ethylene up to a total pressure of 40 atm. The copolymerization reaction was maintained at 90°C and at a pressure of 40 atm for 60 minutes. At the end of the reaction, the reactor was depressurized and it was obtained 365 g of polyethylene (activity  $5 \times 10^6$  g PE/mol M x h x atm) with a Mw of 135.000, MWD of 2, a comonomer content of 1% molar, an bulk density of 0,3 g/cc, a particle medium size of 0,6 mm and a distribution of particles sizes as it is shown in fig. 1.

62  
Table I

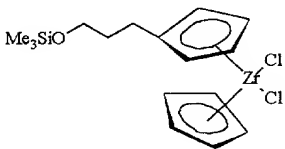
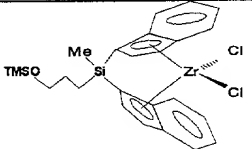
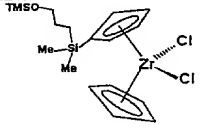
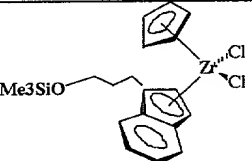
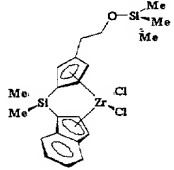
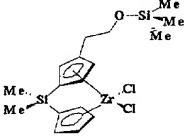
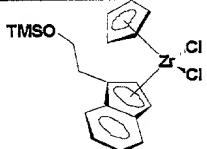
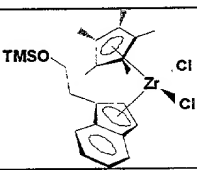
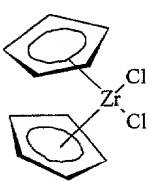
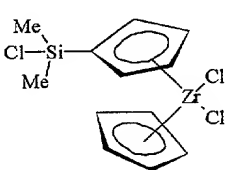
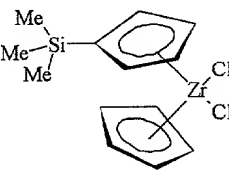
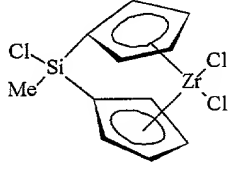
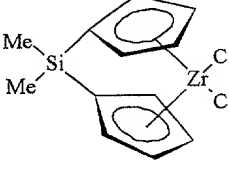
TYPE OF CATALYST	EXAMPLE	METALLOCENE	ACTIVITY x 10 <sup>6</sup>
Homogeneous	20		5,2
Heterogeneous	27		2,4
Homogeneous	-		-
Heterogeneous	30		4,3
Homogeneous	-		-
Heterogeneous	31		0,6
Homogeneous	-		-
Heterogeneous	32		1,1
Homogeneous	-		-
Heterogeneous	33		0,053
Homogeneous	-		-
Heterogeneous	34		0,2
Homogeneous	-		-

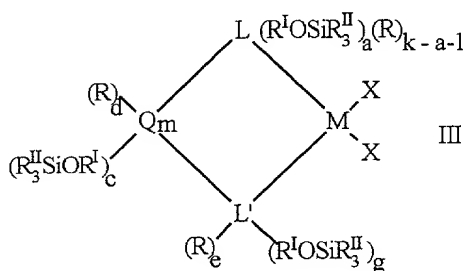
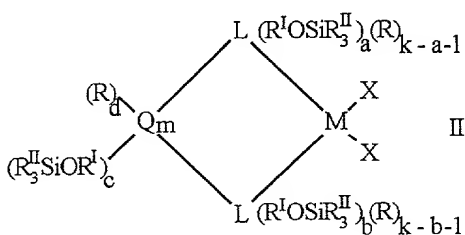
Table 1 continued

Heterogeneous	35		0,2
Homogeneous	23		0,9
Heterogeneous	-		-
Homogeneous	24		8,0
Heterogeneous	36		0,49
Homogeneous	21		10
Heterogeneous	28		1,1
Homogeneous	25		16,9
Heterogeneous	37		1,1
Homogeneous	22		1,3
Heterogeneous	29		0,32
Homogeneous	26		2,9
Heterogeneous	38		0,3

TMSO = Trimethylsiloxy

**CLAIMS**

1. Heterogeneous catalytic system obtainable by reacting a porous inorganic support with an alumoxane and subsequently supporting at least one metallocene compound thereon, characterized in that the metallocene compound is defined by the following general formulas:



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl or benzoindenyl;

each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>;

each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>;

each R<sup>II</sup> is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably R<sup>II</sup> is methyl, ethyl or isopropyl;

each Q is independently selected from B, C, Si, Ge, Sn;

M is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide;

each X is independently selected from: hydrogen, chlorine, bromine,  $OR^I$ ,  $NR^II_2$ ,  $C_1-C_{20}$  alkyl or  $C_6-C_{20}$  aryl;

$L'$  is N or O;

when L is cyclopentadienyl k is equal to 5, when L is indenyl k is equal to 7, when L is fluorenyl or benzoindenyl k is equal to 9, when L is tetrahydroindenyl k is equal to 11 and when L is octahydrofluorenyl, k is equal to 17;

z is equal to 0, 1 or 2;

x is equal to 1, 2 or 3;

y is equal to 1, 2 or 3;

$x + y + z$  is equal to the valence of M;

m is an integer which can assume the values 1, 2, 3 or 4;

a and b are integers whose value ranges from 0 to k-1;

f is an integer whose value ranges from 1 to k;

g is an integer whose value ranges from 0 to 1;

c and e are equal to 0 or 1;

$a + b + c$  is at least 1;

$a + g + c$  is at least 1;

d is equal to 0, 1 or 2;

when Q is B then  $c + d = 1$ ;

when Q is C, Si, Ge or Sn, then  $c + d = 2$ ;

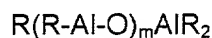
when  $L'$  is N, then  $g + e = 1$ ;

when  $L'$  is O, then  $g = 0$  and  $e = 0$ .

2. Heterogeneous catalytic system according to claim 1 wherein the group  $R^I OSiR^II_3$  is selected from  $CH_2-CH_2-OSiMe_3$ ,  $CH_2-CH_2-CH_2-OSiMe_3$ ,  $CH_2-O-CH_2-OSiMe_3$ ,  $O-CH_2-CH_2-OSiMe_3$ ,  $SiMe_2-CH_2-CH_2-OSiMe_3$ ,  $SiMe_2-OSiMe_3$  or  $SiMe_2-CH_2-CH_2-CH_2-OSiMe_3$ .

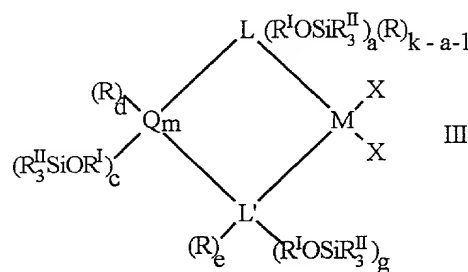
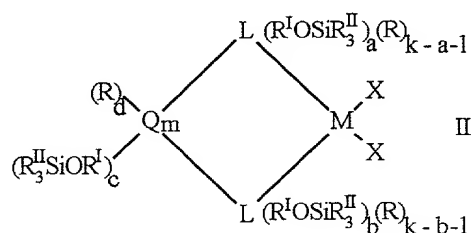
3. Heterogeneous catalytic system according to claims 1-3 wherein M is titanium, zirconium or hafnium.

4. Heterogeneous catalytic system according to claims 1-4 wherein the alumoxane is represented by the formulas:



wherein R is alkyl or aryl group containing from 1 to 20 carbon atoms; n ranges from 1 to 40, and m ranges from 3 to 40.

6. Heterogeneous catalyst system according to claims 1-5 wherein the inorganic support is selected from silica, alumina, silica alumina, aluminium phosphates and mixtures thereof.
7. Heterogeneous catalyst system according to claims 1-6 wherein the content in transition metal is comprised between 0.01 and 3% by weight.
8. Heterogeneous catalyst system according to claim 7 wherein the content in transition metal is comprised between 0.1 and 1% by weight.
9. Process for the polymerization of alpha olefins in slurry or in gas phase characterized by the use of the heterogeneous catalyst system of claims 1-8.
10. Metallocene compounds according to the following formulas:



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl and benzoindenyl;

each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>;

each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron ; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>;

each  $R''$  is independently selected from  $C_1-C_{20}$  alkyl,  $C_3-C_{20}$  cycloalkyl,  $C_6-C_{20}$  aryl,  $C_3-C_{20}$  alkenyl,  $C_7-C_{20}$  arylalkyl,  $C_8-C_{20}$  arylalkenyl or  $C_7-C_{20}$  alkylaryl, linear or branched; preferably  $R''$  is methyl, ethyl or isopropyl;

each  $Q$  is independently selected from B, C, Si, Ge, Sn;

- 5  $M$  is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide; preferably it is titanium, zirconium or hafnium;

each  $X$  is independently selected from: hydrogen, chlorine, bromine,  $OR''$ ,  $NR''_2$ ,  $C_1-C_{20}$  alkyl or  $C_6-C_{20}$  aryl;

$L'$  is N or O

- 10 when  $L$  is cyclopentadienyl  $k$  is equal to 5, when  $L$  is indenyl  $k$  is equal to 7, when  $L$  is fluorenyl or benzoindenyl  $k$  is equal to 9, when  $L$  is tetrahydroindenyl  $k$  is equal to 11 and when  $L$  is octahydrofluorenyl,  $k$  is equal to 17;

$z$  is equal to 0, 1 or 2;

$x$  is equal to 1, 2 or 3;

- 15  $y$  is equal to 1, 2 or 3;

$x + y + z$  is equal to the valence of  $M$ ;

$m$  is an integer which can assume the values 1, 2, 3 or 4;

$a$  and  $b$  are integers whose value ranges from 0 to  $k-1$ ;

$f$  is an integer whose value ranges from 1 to  $k$ ;

- 20  $g$  is an integer whose value ranges from 0 to 1;

$c$  and  $e$  are equal to 0 or 1;

$a + b + c$  is at least 1;

$a + g + c$  is at least 1;

$d$  is equal to 0, 1 or 2;

- 25 when  $Q$  is B then  $c + d = 1$ ;

when  $Q$  is C, Si, Ge or Sn, then  $c + d = 2$ ;

when  $L'$  is N, then  $g + e = 1$ ;

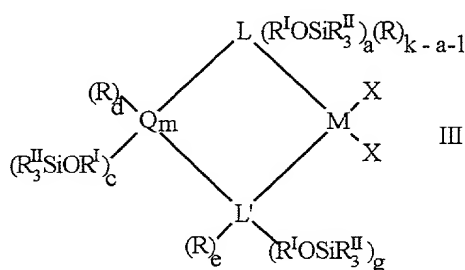
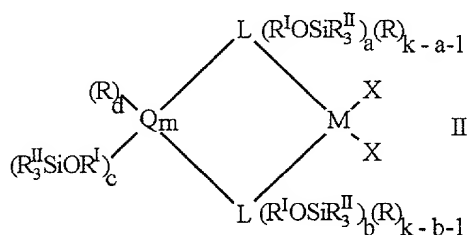
when  $L'$  is O, then  $g = 0$  and  $e = 0$ .

characterized in that at least one  $L$  is a fluorenyl, benzoindenyl or octahydrofluorenyl ring,

- 30 optionally substituted by  $C_1-C_{20}$  alkyl,  $C_3-C_{20}$  cycloalkyl,  $C_6-C_{20}$  aryl,  $C_3-C_{20}$  alkenyl,  $C_7-C_{20}$  arylalkyl,  $C_8-C_{20}$  arylalkenyl or  $C_7-C_{20}$  alkylaryl.

**Abstract:**

The invention relates to heterogeneous catalytic systems obtainable by reacting a porous inorganic support with an alumoxane and subsequently supporting at least one metallocene compound thereon, characterized in that the metallocene compound is defined by the following general formulas:



wherein:

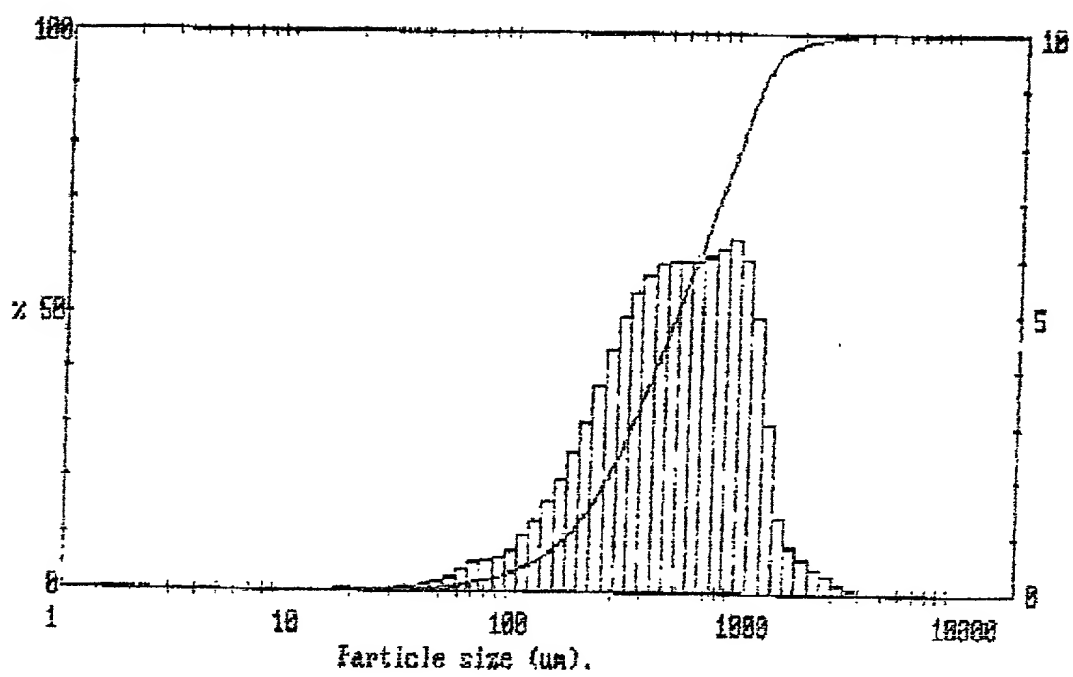
**L**, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl or benzoindenyl; each **R** is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>; each **R<sup>I</sup>**, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>; each **R<sup>II</sup>** is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably **R<sup>II</sup>** is methyl, ethyl, isopropyl; each **Q** is independently selected



5

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Fig. 1



PATENT

Attorney's Docket No. B-3643 617072-2**COMBINED DECLARATION AND POWER OF ATTORNEY****(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL, CONTINUATION, OR CIP)**

As a below named inventor, I hereby declare that:

**TYPE OF DECLARATION**This declaration is of the following type: *(check one applicable item below)*

- ☒ original  
☐ design  
☐ supplemental

**NOTE:** *If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.*

- ☐ national stage of PCT

**NOTE:** *If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION, OR CIP.*

- ☐ divisional  
☐ continuation  
☐ continuation-in-part (CIP)

**INVENTORSHIP IDENTIFICATION**

**WARNING:** *If the inventors are each not the inventors of all the claims an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor *(if only one name is listed below)* or an original, first and joint inventor *(if plural names are listed below)* of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**TITLE OF INVENTION**

CATALYTIC SYSTEMS FOR THE POLYMERIZATION AND COPOLYMERIZATION  
OF ALPHA-OLEFINS.

**SPECIFICATION IDENTIFICATION**the specification of which: *(complete (a), (b) or (c))*

- (a) ☒ is attached hereto.  
 (b) ☐ was filed on \_\_\_\_\_ as ☐ Serial No. 0 / \_\_\_\_\_  
 or ☐ Express Mail No., as Serial No. not yet known, \_\_\_\_\_  
 and was amended on \_\_\_\_\_ *(if applicable)*.

**NOTE:** *Amendments filed after the original papers are deposited with the PTO which contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 CFR 1.67.*

- (c) ☐ was described and claimed in PCT International Application No. \_\_\_\_\_  
 filed on \_\_\_\_\_ as amended under PCT Article 19 (1)  
 on \_\_\_\_\_ *(if any)*.

**ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR**

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code Federal Regulations § 1.56.

☐ In compliance with this duty there is attached an information disclosure statement 37 CFR 1.97.

**PRIORITY CLAIM**

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign applications(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☐ no such applications have been filed.  
(e) ☐ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim.

**EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED WITHIN 12 MONTHS  
(6 MONTHS FOR DESIGN(S)) PRIOR TO THIS U.S. APPLICATION**

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
EPO	98500101.5	27 04 98	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

**ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS  
(6 MONTHS FOR DESIGN(S)) PRIOR TO THIS U.S. APPLICATION**

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POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

Richard P. Berg, Reg. No. 28,145  
Mavis S. Gallenson, Reg. No. 32,464  
Kam C. Louie, Reg. No. 33,008

Richard J. Paciulan, Reg. No. 28,248  
John Palmer, Reg. No. 36,885

(check the following item, if applicable)

☐ Attached as part of this declaration and power of attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO:

c/o LADAS & PARRY  
5670 Wilshire Boulevard, Suite 2100  
Los Angeles, California 90036-5679

DIRECT TELEPHONE CALLS TO:

(Name and telephone number)

(213) 934-2300

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

Full name of sole or first inventor ANTONIO MUÑOZ-ESCALONA LAFUENTE  
Inventor's signature *A. Muñoz Escalona Lafuente*  
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Full name of second joint inventor, if any PILAR LAFUENTE CAÑAS  
Inventor's signature *Pilar Lafuente Cañas*  
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Full name of third joint inventor, if any JOSE SANCHO ROYO  
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Full name of **fourth joint inventor**, if any BEGOÑA PEÑA GARCIA

Inventor's signature 

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Full name of **fifth joint inventor**, if any CARLOS MARTIN MARCOS

Inventor's signature 

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